

2016

# Using Aqueous Soil Extracts to Study Organic Matter Leaching From Soils of Different River Corridor Land Covers in Vermont

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USING AQUEOUS SOIL EXTRACTS TO STUDY ORGANIC MATTER  
LEACHING FROM SOILS OF DIFFERENT RIVER CORRIDOR LAND  
COVERS IN VERMONT

A Thesis Presented

by

Alyson Hampsch

to

The Faculty of the Graduate College

of

The University of Vermont

In Partial Fulfillment of the Requirements  
for the Degree of Master of Science  
Specializing in Geology

October, 2016

Defense Date: August 18, 2016  
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## ABSTRACT

Soils represent an important terrestrial carbon (C) sink, storing up to three times the amount of atmospheric C, however climate and land use changes may transform soils into C sources. River corridor (RC) soils and associated C are at risk to become mobilized by erosion such as bank failure and scour events. Once soil-derived organic C is transferred into the stream, microbial processes and photodegradation of the dissolved, labile (or bioavailable) fractions can lead to the production of CO<sub>2</sub>, which can evade and increase atmospheric CO<sub>2</sub> levels. Because predicted increases in heavy precipitation will likely increase this type of riverine erosion, it is important to better understand the potential for the release of bioavailable C from RCs. One objective of this thesis was therefore to identify and characterize representative samples of soils from a typical Vermont RC for common land covers and simulate the production of dissolved organic matter (DOM) during riverine soil erosion. Field sites representative of typical agricultural and forested land uses were selected based on the analysis of 106 existing samples and resampled multiple times over the summer of 2015. Production of DOM from riverine erosion was simulated using aqueous soil extracts (ASE), where soil and water were shaken at fixed ratios followed by the separation of the extract. To study the characteristics of these extracts (which serve as analogue of stream water after erosion), water extractable C (WEOC) concentrations, water extractable nitrogen, fluorescence properties of DOM, and bioavailability were determined. Results indicated a common, dominantly terrestrial source material for all land covers, but C concentrations and fluorescence properties differed. High but variable amounts of soil organic C and WEOC were observed in agricultural riparian and agricultural stream bank samples, and lower concentrations in agricultural field, forest, forest riparian, and forest stream banks. WEOC bioavailability was high in all agricultural land covers and low in forested land covers.

Because this study is the first in which ASE are used as analogues for stream water after riverine erosion, a second objective was to test laboratory methods used in this study for their effect on WEOC, fluorescence properties, and bioavailability. Specifically, the effects of soil drying, soil storage, and the effects of the extraction solution were tested. For this, ASE were prepared from soils that were field moist, dried, and after two years of storage. In addition, dried soils were extracted using different solutions including a salt solution, river water, and double deionized (DDI) water. Results indicated WEOC concentration and microbial humic-like fluorescence from extracts of dried soils were higher than those in extracts of field moist soils, while WEOC concentration and microbial humic-like fluorescence was highest in extracts of soils stored long term. In addition, the bioavailability of WEOC was higher in dried soils than field moist soils. The extraction solutions of DDI water and river water produced DOM with similar fluorescence properties, while the salt solution extracted a different, less humified pool of C. Overall, the ASE methods used in this study are effective in simulating stream bank erosion and subsequent C release into stream water, however the effects of drying the soils need to be considered when assessing DOM.

## **ACKNOWLEDGEMENTS**

I would like to thank my advisor, Julia Perdrial, for her support and guidance throughout this endeavor. Her help and steady presence has been much appreciated. Many thanks also to my committee, including Don Ross and Paul Bierman for providing insight and comments as this project progressed.

David Jaeger and Malayika Cincotta provided wonderful assistance in the field over the summer, and are much appreciated. They, as well as Lauren Jones, Ingrid Evans, Ashley Weltz, and Mae Kemsley were also a pleasure to work with in the lab.

Thanks to all of the geology graduate students I had the opportunity to spend time with for making this experience so enjoyable. And finally, thanks to all of my family and friends for their unwavering support.

## TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	iii
LIST OF TABLES .....	vi
LIST OF FIGURES .....	vii
CHAPTER 1: INTRODUCTION.....	1
1.1 Soil Organic Matter As a Source of Stream Water DOC.....	1
1.2 Climate Change Driving River Corridor Dynamics .....	1
1.3 Research Hypotheses and Objectives.....	2
CHAPTER 2: BACKGROUND AND LITERATURE REVIEW.....	4
2.1 Soil Organic Carbon Stability.....	4
2.2 Typical River Corridor Soils: From a Terrestrial Sink to An Aquatic Source? .....	6
2.3 Spectral Analysis of DOC and Bioavailability .....	7
CHAPTER 3: CHARACTERISTICS OF DISSOLVED ORGANIC MATTER LEACHED FROM SOILS OF REPRESENTATIVE LAND COVERS IN A VERMONT RIVER CORRIDOR.....	9
Abstract.....	9
3.1 Introduction.....	10
3.1.1 Carbon in River Corridor Soils.....	10
3.1.2 Land Cover Effects on Soil Carbon .....	11
3.1.3 Field Site.....	13
3.2 Materials and Methods.....	15
3.2.1 Sampling Methods.....	15
3.2.2 Solid Phase Analysis.....	17
3.2.3 Aqueous Soil Extracts .....	17
3.2.4 Aqueous Analyses .....	17
3.2.5 Incubations.....	19
3.2.6 Statistical Analyses .....	20
3.3 Results.....	24
3.3.1 TOC and WEOC By Land Cover .....	24
3.3.2 Spectral Indices and PARAFAC Components .....	27
3.3.3 Incubations.....	31
3.3.4 Temporal and Depth Variability .....	36
3.4 Discussion.....	38
3.4.1 Temporal and Depth Variability of Organic Matter.....	38
3.4.2 Carbon Characteristics and Processes .....	38
3.4.3 Bioavailability Using Spectral Methods: A Valid Approach for Soils? .....	43
3.4.4 The Relationship Between SOC, WEOC, and Bioavailable C .....	44
3.5 Conclusions .....	45
3.6 References .....	46
CHAPTER 4: THE EFFECT OF SOIL STORAGE AND AQUEOUS EXTRACTION METHODS ON WATER EXTRACTABLE CARBON (WEOC) CHARACTERISTICS.....	52
Abstract.....	52
4.1 Introduction.....	53
4.2 Materials and Methods.....	56

4.2.1 Field Sampling .....	56
4.2.2 Laboratory Analyses .....	58
4.2.3 Statistical Analyses .....	63
4.3 Results.....	63
4.3.1 Soil Drying and Storage .....	63
4.3.2 Impact of Extract Solution Composition on WEOM Characteristics .....	69
4.4 Discussion.....	71
4.4.1 Soil Drying In the Laboratory.....	71
4.4.2 Effects of Extract Solution .....	73
4.5 Conclusions .....	75
4.6 References .....	76
CHAPTER 5: CONCLUSIONS.....	79
REFERENCES .....	80
APPENDIX I: PRELIMINARY DATA USED FOR SAMPLE SITE SELECTION .....	90
APPENDIX 2: CARBON BY DEPTH.....	93

## LIST OF TABLES

Table 3.1. PARAFAC component comparison and identification. ....	23
Table 3.2. Mean and standard deviation of PARAFAC components and spectral indices by land cover. ....	28
Table 3.3. Bioavailability of WEOC (aqueous extracts) and TOC (dried soil) of the composite soil samples from the top 15 cm of the soil column. ....	32
Table 3.4. Bioavailability of WEOC from composite soil samples from the top 60 cm of the soil column. ....	33

## LIST OF FIGURES

Figure 3.1. The Mad River corridor in northern Vermont. The agricultural and forested sample sites are shown. ....	14
Figure 3.2. Excitation and emission loadings of the four components from the PARAFAC model, compared to loadings from Murphy et al. 2011. C1 and C2 from this study are similar to their G-1 and G2, respectively. C3 from this study has no equivalent and C4 from this study is red-shifted relative to their G7. ....	22
Figure 3.3. TOC and WEOC of the soils by sampling depth. ....	24
Fig. 3.4 TOC by land cover (n = 71). Boxplots show median and upper and lower quartiles in the box and range as extended lines. Land covers with different letters denote pairs of means that are significantly different ( $p < 0.05$ ). ....	25
Fig 3.5 WEOC by land cover (n = 71). Boxplots show median and upper and lower quartiles in box, range as extended lines. Land covers with different letters denote pairs of means that are significantly different ( $p < 0.05$ ). ....	26
Figure 3.6. WEON by land cover (n = 71). Boxplots show median and upper and lower quartiles in box, range as extended lines. No land covers have significantly different WEON ( $p > 0.05$ ). ....	26
Figure 3.7. Correlation between carbon characteristics and WEOC of aqueous soil extracts. Squares represent samples for which the aqueous extract was incubated and triangles represent soils for which both the aqueous extract and the soil were incubated. ....	29
Figure 3.8. PARAFAC components regression with $SUVA_{254}$ (aromaticity) and HIX (degree of humification). ....	31
Fig. 3.9. PARAFAC components C1 and C4 vs. WEOC bioavailability, with $R^2$ (correlation) and p-value (statistical significance) shown. ....	33
Fig. 3.10. WEOC and TOC vs. bioavailability of C in aqueous extracts, with $R^2$ (correlation) and p-value (statistical significance) shown. ....	34
Figure 3.11. C respired from incubations of soil at 70% of field capacity over 81 days. ....	35
Figure 3.12. WEOC and PARAFAC components on each sampling date. ....	37
Figure 4.1. (a) Location of the Mad River watershed in the Winooski watershed in northern Vermont. (b) The agricultural site is located close to Waitsfield Elementary. (c) The forested site is located close to Riverside Park. ....	57
Figure 4.2. Sample splits and corresponding laboratory analyses. ....	62
Figure 4.3. TOC comparison between archived soil and newly sampled dry soil. Boxplots show median and upper and lower quartiles in box, range as extended lines. ....	64
Figure 4.4. Water extractable organic C (WEOC) compared to total organic C (TOC) for aqueous extractions of dried soil (red line) and field moist soil (blue line). ....	65
Figure 4.5. Water extractable organic C (WEOC), PARAFAC components, HIX, $SUVA_{254}$ , and FI comparisons between archived soil, newly sampled dry	



soil, and newly sampled moist soil. Boxplots show median and upper and lower quartiles in box, range as extended lines. ....	67
Figure 4.6. Respired C expressed as percentage of dry and moist soil. Boxplots show median and upper and lower quartiles in box, range as extended lines. ....	68
Figure 4.7. FI, HIX, and absorbance at 254 nm, of agricultural and forested soils with three extract solutions. ....	70
Figure A2. TOC by land cover for all archived soils, archived soils from the sites selected for resampling (Waitsfield Elementary for agricultural and Riverside Park for forested), and resampled soils (at Waitsfield Elementary and Riverside Park). Boxplots show median and upper and lower quartiles in box, range as extended lines. ....	91
Figure A3. WEOC by land cover for all archived soils, archived soils from the sites selected for resampling (Waitsfield Elementary for agricultural and Riverside Park for forested), and resampled soils (at Waitsfield Elementary and Riverside Park). Boxplots show median and upper and lower quartiles in box, range as extended lines. ....	92
Figure A4. TOC of the soils by sampling depth and land cover.....	93
Figure A5. WEOC of the soils by sampling depth and land cover.....	94

## **CHAPTER 1: INTRODUCTION**

### **1.1 Soil Organic Matter As a Source of Stream Water DOC**

Soils represent an important terrestrial carbon (C) sink, storing up to three times more C than the atmosphere (Lal 2003). Soil organic carbon (SOC) is derived mainly from leaf litter and root residues (Zech et al., 1997) and can be chemically and microbiologically transformed but also stabilized and stored for hundreds to thousands of years (Blazewski et al., 2005). This material is also an important source of dissolved organic carbon (DOC), the most mobile form of organic C in soils (Kaiser and Zech, 1997) that is easily accessed and processed by microorganisms or photodegraded (Ishii and Boyer, 2006). Soils in river corridors (RCs), which includes the riverbed and the parts of the floodplain that interact with the stream, are affected by their close proximity to the stream and can potentially source DOM to the streams when flushed or scoured.

### **1.2 Climate Change Driving River Corridor Dynamics**

Due to several factors, watersheds in Vermont are likely at risk of transforming from a C sink to a C source. Firstly, glacial till and lacustrine deposits were formed throughout Vermont during the last glacial maximum (Stewart and MacClintock, 1969; Field Geology Services, 2007), resulting in large stores of easily transportable, unconsolidated material. Secondly, deforestation during early settlement in Vermont brought large amounts of sediment to the RC which is, due to subsequent reforestation, eroding (Albers, 2000; Bierman et al., 2005; Field Geology Services, 2007).

Lastly, climate change projections for the Northeast in general, and Vermont specifically, indicate an increase in heavy precipitation, resulting in more frequent flood

events (Frumhoff et al., 2007; Galford et al., 2014, Guilbert et al., 2015) that could increase riverine erosion and potentially transform floodplains from C sinks to sources. Heavy rain events, such as the one resulting from the Irene disaster in 2011, are projected to increase. Stream bank erosion and scour during these events result in the transfer of soil and sediments, along with associated C, into the stream (Nanson and Croke, 1992; Hupp and Osterkamp, 1996), while DOC can be flushed through the soil column, followed by lateral transport to the stream channel (Schelker et al. 2013, Terajima and Moriizumi 2013). In the stream, C becomes available to microbes for processing, introducing more CO<sub>2</sub>, a greenhouse gas, into the atmosphere (Lal, 2003; Perdrial et al., 2014). Therefore determining the characteristics, especially the mobility and bioavailability, of SOC in near stream soils is of great importance.

### **1.3 Research Hypotheses and Objectives**

The following hypotheses were tested: 1) SOC content (/kg soil), water extractable organic carbon (WEOC) concentration (mg/kg of soil) and C bioavailability (% respired C) vary systematically with land cover and 2) these differences are controlled by molecular scale characteristics that can be resolved by fluorescence spectroscopy. Variations in these parameters were identified by land cover, because RCs in VT typically have a mixed land use of forested and agricultural.

Another objective was to test laboratory methods used in this study, including the effect of soil drying, soil storage, and the choice of extraction solution, for their effect on WEOC, fluorescence properties, and bioavailability. It was hypothesized that dried soils release higher amounts of C upon water extraction than field moist soils and that aqueous

extractions using deionized water are similar to those using river water, and can be used to simulate soil interactions with river water (Hypothesis 3). A combination of laboratory analogues for DOC production from bank scour and statistical analyses were used to test all three hypotheses.

## CHAPTER 2: BACKGROUND AND LITERATURE REVIEW

### 2.1 Soil Organic Carbon Stability

Organic carbon (C) enters the soil fabric by decomposition of leaf litter, other organic detritus, and from fine roots in the soil (Ussiri and Johnson 2007, Fisk et al. 2010). As these materials decompose and the more bioavailable forms of C are used, less reactive and less biologically available types of C accumulate (Ussiri and Johnson 2003). The traditional view on soil organic carbon (SOC) stability (or lability) includes the inherent recalcitrance of certain molecules. For example, complex and aromatic molecules are hypothesized to be more difficult to degrade for most soil microorganisms, while simpler molecules including simple carbohydrates, organic acids, and proteins are more bioavailable (Heitkamp and Cerniglia, 1987; Marschner and Kalbitz, 2003).

However, today SOC stability is considered a function of a mixture of aforementioned chemical properties as well as biological, physical, and environmental factors (Schmidt et al., 2012). *Biological* processes in soils lead to the decomposition of organic matter and alter organic matter composition and bioavailability (Lamparter et al. 2009, Marinari et al. 2010), often mobilizing C. Soil respiration (i.e. respiration of soil organisms and roots) plays an important role and leads to the transformation of organic C to CO<sub>2</sub>. When C is flushed from the soil into the stream, its availability to microorganisms increases.

The *physical* stabilization of SOC is hypothesized to lead to long term preservation of C in soils and includes the sorption and complexation of C with soil minerals (Zech et al., 1997; Bullinger-Weber et al., 2014; Herbrich et al., 2015). Clay content and iron oxide content of soils therefore strongly affects SOC stabilization

(Bullinger-Weber et al., 2014). For example, sorption onto clay particles protects the SOC from microbial activity, decreasing C bioavailability while increasing residence time in the soil (Zech et al., 1997). Iron and other metals in soils complex with the organic material, resulting in relatively stable, recalcitrant organo-mineral complexes (Marschner and Kalbitz, 2003; Bullinger-Weber et al., 2014). Interaction between these different soil components forms aggregates that physically protect the C from microbial activity (Jastrow, 1996; Lehmann et al., 2007; Verchot et al., 2011; Dungait et al., 2012).

Last but not least, *environmental factors* are important. For example, several studies have recorded how temperature and moisture changes, mainly from precipitation, control soil processes, using soils at different elevations within a catchment (Johnson et al. 2000, Groffman et al. 2009) or vegetation removal (McLaughlin et al. 2012, Schelker et al. 2013, Dib et al. 2014). Increased temperature and increased moisture generally increase organic C export as soil respiration and microbial activity are stimulated and increase (Zech et al. 1997, Johnson et al. 2000, Groffman et al. 2009).

River corridors (RCs) represent a very specific setting where C source and sink dynamics are additionally linked to riverine erosion and deposition processes (Cierjacks et al. 2011). Overbank flow events cause water to move slowly over the floodplain, depositing particulate organic C along with deposited sediment (Wohl et al. 2012), which has already experienced C processing in previous soils or in the stream. Once deposited in the floodplain, C may be stored long-term or processed further. In contrast, bank failure can result in the loss of entire sections of soil or of certain horizons, altering the soil structure (Nanson and Croke 1992, Hupp and Osterkamp 1996, Lal 2003) and impacting SOC stability.

## **2.2 Typical River Corridor Soils: From a Terrestrial Sink to An Aquatic Source?**

Soil development is affected by several factors, including parent material, age, topography, and climate (Jenny, 1941; Ciolkosz et al., 1989). RC soils are no exception but are additionally strongly affected by flooding and are usually classified as alluvial. Horizonation (i.e. the development of layers that have distinct texture and composition) is mostly driven by the top down delivery of new sediment (Nanson and Croke 1992, Hupp and Osterkamp 1996, Lal 2003, Blazejewski et al. 2009, Lewin and Ashworth 2014), which episodically buries developing organic horizons (Blazejewski et al. 2009, Ricker et al. 2013). These often irregularly layered lenses of buried organic rich horizons contain large quantities of bioavailable organic C and nutrients at several depths in the soil profile (Gurwick et al. 2008, Blazejewski et al. 2009, Ricker et al. 2013, James, 2013). The development of RC soils is therefore limited and Entisols (i.e. soils that have limited horizon development) are a common soil order in RCs (Soil Survey Staff, 2010).

Carbon is typically physically protected and quite stable when bound to mineral soil particles (Zech et al., 1997; Bullinger-Weber et al., 2014; Herbrich et al., 2015); therefore buried horizons represent a C sink. However scour and bank failure close to the river can result in the loss of soil, sometimes the entire vertical profile (Nanson and Croke 1992, Hupp and Osterkamp 1996, Lal 2003), and may liberate C from these locations. Such flushing of SOC from soils produces DOC, which is typically quite bioavailable (lacking most aforementioned stabilization mechanisms) and more readily degraded than particulate forms. Resulting increases in inorganic, riverine C augments  $P_{CO_2}$ , which leads to  $CO_2$  evasion if stream  $P_{CO_2}$  exceeds that of the atmosphere (Lauerwald et al., 2013; Moody et al., 2013; Perdrial et al., 2014).

### 2.3 Spectral Analysis of DOC and Bioavailability

Spectral methods such as absorbance and fluorescence spectroscopy are often applied to study the molecular properties of dissolved organic matter (DOM) in streams (McKnight et al., 2001; Cory et al., 2011) and soils (Pedrial et al., 2012; Gabor et al., 2015). The methods require minimal sample preparation and several empirical indices can be readily obtained. For example, the specific UV absorbance ( $SUVA_{254}$ ) is the C-normalized absorbance and serves as an indicator for DOM aromaticity (Weishaar et al., 2003). The humification index (HIX) is based on emission intensities at 435-380 nm divided by the area at 300-345 nm, each at excitation 254 nm, and correlates with the degree of polycondensation (often interpreted as humification) of DOM (Zsolnay et al., 1999; Ohno, 2002). To determine the precursor material of the DOM, the fluorescence index (FI) has been used to differentiate between microbial and terrestrial sources (McKnight et al., 2001; Cory and McKnight, 2005). These indices have also been correlated with DOM bioavailability. For example, high  $SUVA_{254}$  is correlated with low bioavailability (Kujawinski et al., 2004; Kim et al. 2006), while the low H/C ratio of a highly humified extract may be related to low bioavailability (Zsolnay et al., 1999).

In addition to these indices, the excitation and emission matrixes (EEMs) from fluorescence spectroscopy can also be “deconvoluted” using a parallel factor (PARAFAC) analysis that finds components in a n-way dataset (Stedmon and Bro 2008). Comparing components with data from the literature and scans of known materials such as amino acids provides meaning to these statistical results. Typical components described in the past comprise humic acid-like, fulvic acid-like, and protein-like components that are sometimes linked to carbon lability, biodegradation, and



bioavailability (Kujawinski et al. 2004; Kim et al. 2006; Fellman et al., 2010; Ishii and Boyer, 2012).

While fluorescence derived indices can be very useful, they do not provide a direct measure of DOM bioavailability. It is therefore advised to compare fluorescence indices and PARAFAC results with direct measures of respired C amounts as determined using incubations (Boyer and Groffman, 1996; Townsend et al., 1997; Marschner and Kalbitz, 2003; McDowell et al., 2006; Reid et al., 2012; Birge et al., 2015).

# **CHAPTER 3: CHARACTERISTICS OF DISSOLVED ORGANIC MATTER LEACHED FROM SOILS OF REPRESENTATIVE LAND COVERS IN A VERMONT RIVER CORRIDOR**

(to be submitted to the Soil Science of America Journal)

## **Abstract**

Soils represent an important terrestrial carbon (C) sink, storing up to three times more C than the atmosphere, however climate and land use changes may transform soils into C sources. River corridor (RC) soils and associated C are at risk to become mobilized by erosion such as bank failure and scour events. Once soil-derived organic C is transferred into the stream, microbial processes and photodegradation of the dissolved, labile (or bioavailable) fractions can lead to the production of CO<sub>2</sub>, which can evade and increase atmospheric CO<sub>2</sub> levels. The likelihood of this type of erosion is augmented by the glacial history, land use history, and the predicted increases in heavy precipitation in the North East, hence the need to investigate the potential for the release of bioavailable C from RCs. For this, field sites representative of typical agricultural (pasture) and forested land uses were selected and sampled multiple times over the summer of 2015. Production of dissolved organic matter (DOM) from riverine erosion was simulated using aqueous soil extracts (ASE) from these RC soils. To study the characteristics of these extracts, water extractable organic C (WEOC) concentrations, water extractable nitrogen, dissolved organic matter (DOM) fluorescence properties and bioavailability were determined. Results indicated a common, dominantly terrestrial source material for all land covers, but C concentrations and fluorescence properties differed with land cover. High but variable amounts of soil organic C and WEOC were observed in agricultural riparian and agricultural stream bank samples, and lower concentrations in agricultural field, forest, forest riparian, and forest stream banks. WEOC bioavailability was high in all agricultural land covers and low in forested land covers. These results indicate that DOM derived from different locations within a RC varies greatly, limiting our current abilities to constrain the risk for RC to act as a C source in the future.

### **3.1 Introduction**

#### **3.1.1 Carbon in River Corridor Soils**

River corridor (RC) soils are greatly affected by the interaction with the stream, where C is leached away during high flows and sediment is deposited (Cierjacks et al., 2011). This dynamic can limit the development of alluvial soils but can also add complexity by burying organic rich horizons with large quantities of bioavailable organic C at depth (Gurwick et al., 2008; Blazejewski et al., 2009; Ricker et al., 2013). Carbon is typically physically protected and quite stable when bound to mineral soil particles (Zech et al., 1997; Bullinger-Weber et al., 2014; Herbrich et al., 2015) and buried horizons represent a C sink. However scour and bank failure close to the river can result in the loss of soil, sometimes the entire vertical profile (Nanson and Croke 1992, Hupp and Osterkamp 1996, Lal 2003), and may liberate C from these locations. Such flushing of SOC from soils produces DOC, which is typically quite bioavailable (lacking most aforementioned stabilization mechanisms) and more readily degraded than particulate forms. Resulting increases in inorganic, riverine C augments  $P_{CO_2}$ , which leads to  $CO_2$  evasion if stream  $P_{CO_2}$  exceeds that of the atmosphere (Lauerwald et al., 2013; Moody et al., 2013; Perdrial et al., 2014).

Carbon dynamics in RCs are bound to change because of changes to the climate system, particularly increased flooding (Frumhoff et al., 2007; Galford et al., 2014, Guilbert et al., 2015), which leads to increased erosion, scour and bank failure, and creates new flow paths that may liberate C.

### **3.1.2 Land Cover Effects on Soil Carbon**

Common land cover and land use (hereafter together referred to as land cover) classes in Vermont RCs are agricultural and forested, which transition into riparian vegetation and bare stream bank with increasing proximity to the stream. These land covers have an important influence on C processing and storage because of the different C inputs from vegetation, interactions with the stream, and disturbances associated with a given land cover class. For example, agricultural fields often experience tillage and crop harvest, both affecting soil C storage (Murty et al., 2002). Crop tillage and harvest typically reduces the total SOC, but may increase water extractable organic carbon (WEOC) due to the type of litter introduced to the soil (Boyer and Groffman, 1996), increasing the amount of bioavailable dissolved organic matter (DOM) from agricultural soils relative to forest soils (Kalbitz et al. 2003). In contrast, forest soils receive large inputs from leaf litter increasing the C content (Batjes, 1996) and because forest soils experience less drying than agricultural soils, due to protection by vegetation (Kaiser et al., 2015) C protecting aggregates may remain more intact.

Stream banks adjacent to either land cover accumulate large amounts of sediments from deposition at unequal intervals due to their proximity to the river (Jacobson et al., 2003), therefore stream banks are more likely to accommodate aforementioned buried horizons and erosional and depositional processes may overall dominate over soil forming processes. Stream banks also contribute a large amount of sediment and associated C to rivers due to the proximity to the river. Changes in the sediment flux of the river system can lead to migration and modification of the stream

bank (James, 2013; Lewin and Ashworth, 2014) overall increasing the risk of stream bank erosion (Hupp et al., 2015).

Riparian zones represent the interface between terrestrial and aquatic systems in RCs, and exert a strong control over C exchange within the system (Sommer 2006) (Fig. 1). Similarly to stream banks, riparian areas are influenced by periodic flooding and associated sediment delivery, but are vegetated and receive C inputs and greater soil stability from this vegetation (Brooks and Kyker-Snowman 2009). Riparian areas tend to have high soil moisture and therefore create favorable environments for microbial processes (Lohse et al., 2009) but exhibit a great variability in C distribution and processing rates (Fahey et al. 2005). Although riparian areas comprise only a small portion of the RC by area, a disproportionately high amount of C is typically stored in these zones (McLaughlin et al. 2011, Ricker et al. 2013) making them influential in the C dynamics of the RC.

We hypothesize that these, land cover specific, drivers for C inputs and cycling drive amount of SOC and the characteristics of WEOC. Accordingly SOC is expected to be high and heterogeneous in forest land cover because of high, but variable leaf litter inputs producing lower bioavailability WEOC. Agricultural SOC amount is expected to be low and homogenous across samples due to past harvest and tilling. However, manure application could lead to higher bioavailability DOM production from these soils. Stream banks are expected to contain C-poor sediment while riparian areas contain high amounts of SOC. To test these hypothesis a combination of field sampling of representative sites in a typical Vermont RC (the Mad River), aqueous soil extracts as a laboratory analogue for riverine WEOC production, and absorbance and fluorescence

spectroscopy to characterize WEOC characteristics and bioavailability (additionally assessed with incubations) were used.

### **3.1.3 Field Site**

The Mad River corridor is located in northern Vermont (Fig. 3.1) was selected for this study because it represents a typical New England alluvial RC with a stream incising into legacy sediments (James, 2013; Field Geology Services, 2007). Geologically this area is part of the Green Mountains, which are composed of metamorphosed rocks, including gneiss and schist (Ratcliffe et al. 2011). Glaciation during the last glacial maximum about 20,000 years ago left unconsolidated glacial till and lacustrine deposits as the most abundant surficial material in the Mad River valley (Stewart and MacClintock, 1969; Field Geology Services, 2007).

While the region was initially forested, deforestation for agricultural uses was widespread for both crops and animal grazing during early settlement. This deforestation greatly enhanced the sediment flux into the river system in the entire region, including the Mad River corridor (Field Geology Services, 2007). Passive reforestation since the late 1800s reduced the sediment load to the river, leading to the typical incising streams observed today (Albers, 2000; Bierman et al., 2005; Field Geology Services, 2007).

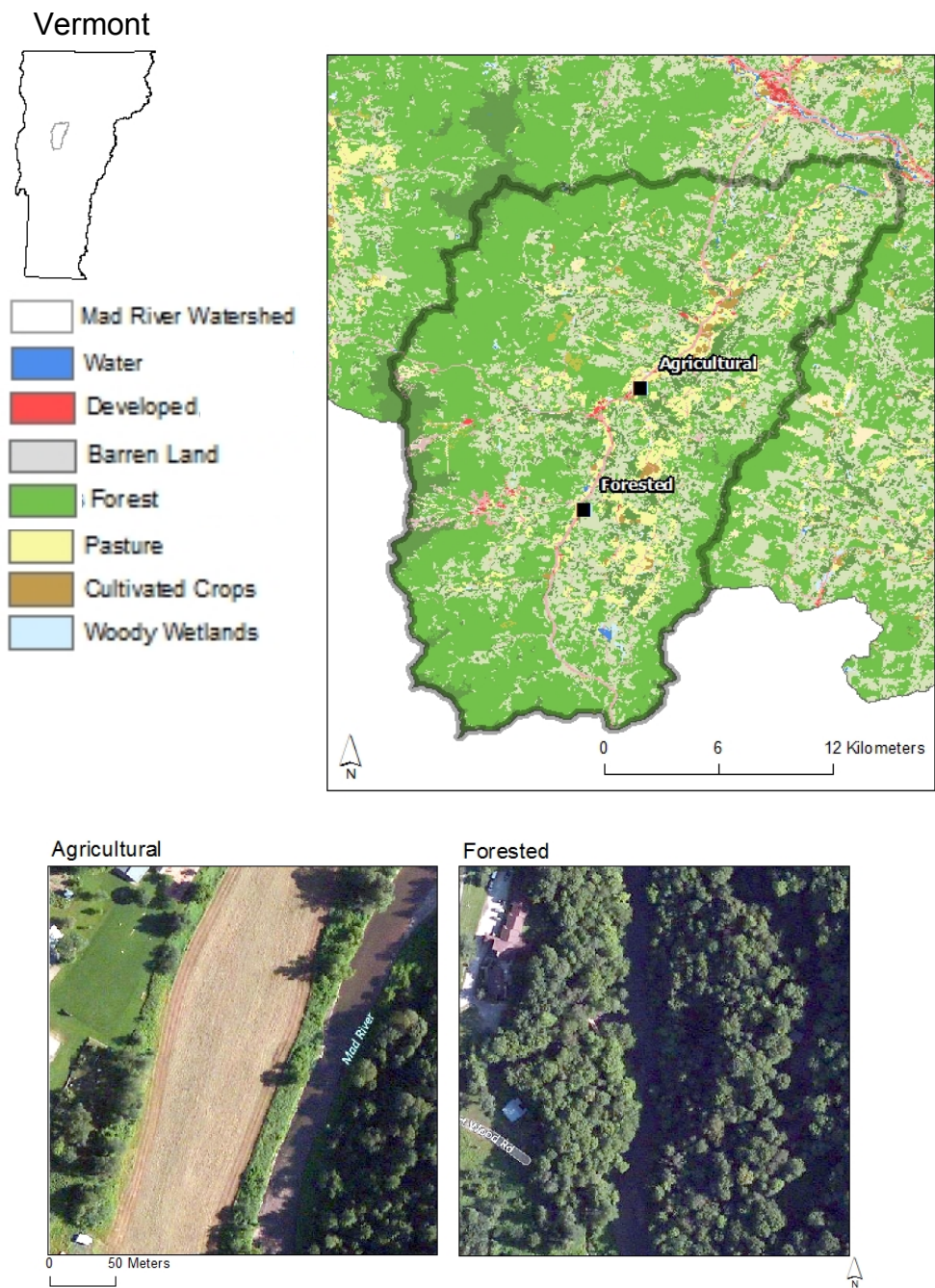


Figure 3.1. The Mad River corridor in northern Vermont. The agricultural and forested sample sites are shown.

The drainage area is about 370 km<sup>2</sup> of mostly forested (83%) land cover, however the RC consists of mixed forested and agricultural land covers. Flooding associated with precipitation events impacts the Mad River and its corridor: since monitoring began in 1928, there have been at least four large floods that exceeded bankfull discharge of 4,391 cfs (Field Geology Services, 2007), including the recent tropical storm Irene, suggesting that the Mad River will be further impacted by flooding during future storm events. Eroded sediment is often deposited in the RC as well as within the channel, where it is available for transport during high flows. Gravel bars are common, especially where bedrock constrictions or channel straightening affect flow velocity and sediment capacity of the stream (Field Geology Services, 2007).

Efforts to control flooding and overbank flow include channel straightening and channelization, which additionally contribute to increased incision rates (Field Geology Services, 2007). Sample sites chosen for this study avoided these channelized or otherwise altered areas. The lack of riparian buffer zones in many sections of the RC has also contributed to the erosion and channel widening (Field Geology Services, 2007) and additionally seems to increase nutrient loading (Lowrance et al., 1984).

## **3.2 Materials and Methods**

### **3.2.1 Sampling Methods**

Previously collected soil samples from the Mad River corridor (collected in 2013 as part of VT EPSCoR RACC) were aqueously extracted and analyzed for DOM quantity and characteristics. These results were used to select two sites representative of agricultural and forested land uses (Appendix 1). The forested site is established on



secondary growth forest at Riverside Park in Warren (44.138°, -72.846°) and the agricultural site is established on a hayfield and pasture in Waitsfield (44.194°, -72.819°) (Fig. 3.1).

In order to test for the importance of land cover dependent soil characteristics, these sites were sampled several times over the summer 2015 (06/4, 06/23, 07/08, 08/04 and 08/12) using replicate transects for each sampling day. Each transect included samples of the stream bank, the riparian area, and the far stream area (10 m distance from the river) that is not constantly interacting with the channel. All locations were sampled at three depths (0-15 cm, 15-30 cm, and 30-60 cm or refusal). The last two sets of samples (08/04 and 08/12/2015) were collected as composite samples to allow for more laborious tests especially the incubations on representative soils. For this, ten samples from each land cover type were collected, combined, and mixed in the lab, resulting in one homogenized sample for each land cover and sampling day.

### **3.2.2 Solid Phase Analysis**

Total organic C (TOC), representing the total solid phase C in g/kg soil, was measured for all soil samples using an elemental analyzer (CE instruments NC 2500, Lancashire, UK) on dried, 2 mm sieved soils that were ground in a ball mill. Around 0.2 mg of each sample was transferred to tin capsules (Costech, Valencia, CA, USA) and combusted at 1800° C.

### **3.2.3 Aqueous Soil Extracts**

Aqueous soil extracts (ASE) were used as an analogue for river water that received C input from near stream soils and sediment after an erosional event. Dried soils were sieved (<2mm) and extracted with double deionized water (DDI) (see chapter 4 for details) at a solid/liquid ratio of 1:5 and shaken on a reciprocal shaker (Eberbach, Ann Arbor, MI, USA) for 1 hour, followed by centrifugation to remove the suspended particles (Perdrial et al., 2012; Gabor et al., 2015). About half of the supernatant was filtered through a 0.45 µm nylon filter (Merck Millipore Ltd., Cork, Ireland) into DI washed glass vials for inorganic C analysis and into 15ml metal free tubes for anion and pH analyses. The other half of the solution was filtered through combusted 0.7 µm glass fiber filter (Whatman GF/F, Buckinghamshire, UK) into combusted amber glass vials for the analysis of WEOC and total dissolved nitrogen (TDN) concentrations and spectroscopic WEOM analyses.

### **3.2.4 Aqueous Analyses**

DOC and DIC concentrations were determined by infrared detection of CO<sub>2</sub>, after catalytic oxidation of DOC at 720°C and acidification of DIC, respectively using a

Shimadzu Total Organic C Analyzer (Columbia, MD, USA). TDN was determined using catalytic thermal decomposition at 720° C and chemiluminescence detection. Anions were measured using ion chromatography (IC) (Dionex, Sunnydale, CA) to determine nitrate ( $\text{NO}_3^-$ ) concentration as proxy for inorganic N. Organic nitrogen was then calculated by subtracting  $\text{NO}_3^-$ -N from TDN.

Absorbance and fluorescence spectroscopy were used to characterize WEOC using a Horiba Aqualog Fluorescence Spectrometer (Horiba, Irvine CA, USA). Filtered undiluted samples were measured to determine absorbance at 254 nm and to calculate specific UV vis absorbance ( $\text{SUVA}_{254}$ , a measure for DOM aromaticity (Weishaar et al. 2003). Absorbance intensity at 254 nm was normalized to DOC (in mg/L) and multiplied by 100 to account for conversions from the cell path length.

Absorbance at 254 nm was also used to determine the necessary dilution factor for the collection of fluorescence analysis to reach an absorbance between 0.1 and 0.3 to reduce the inner filter effect (Ohno et al, 2002; Miller et al., 2009). Fluorescence emission was collected at range of EM 212.62-619.21 (increment of 3.336 nm) over the excitation range of EX 240-600 nm (increment of 3 nm) to generate excitation emission matrices (EEMs). Blanks of ultrapure water (18.2 M $\Omega$  cm-1) were measured daily and subtracted from the sample EEMs, Intensities were normalized to the area under the water Raman peak at 350 nm and inner filter effects were additionally corrected based on UV absorbance data (Ohno, 2002; Miller et al., 2009).

Several indices were calculated from fluorescence data using Matlab R2014b. The FI provides an indication about the source of the DOC (microbial or terrestrial) (McKnight et al., 2001; Cory and McKnight, 2005) and is used constrain sources of

WEOC by land cover. FI is calculated as the intensity at emission 470 nm divided by intensity at 520 nm, each at excitation 370 nm. The HIX is a measure of the humification (or degree of polycondensation) of DOC (Zsolnay et al., 1999; Ohno, 2002) and is calculated as the area under emission 435-380 nm divided by the area at 300-345 nm, each at excitation 254 nm.

### **3.2.5 Incubations**

Composite samples were used for incubations. To test whether these samples represent the average soil of a given land cover (Nichols et al., 2002; Jungers et al., 2009) all results were compared to previously collected data.

Bioavailability of SOC was determined through incubations of both ASE and the soils directly, for the composite samples collected in August. For WEOC, bioavailability was determined on ASE by incubation using established methods (McDowell et al., 2006). ASE were prepared as previously described and 50 mL of the extract was combined with 0.5 mL of an inoculum in combusted glass flasks. The inoculum was prepared with 0.6 g total of soils from each land cover in 74.4 mL water hand shaken for one minute and allowed to rest for 24 hours, after which the supernatant was removed and used as the inoculum. The inoculated extracts were then transferred into Erlenmeyer flasks, covered partially with parafilm to allow for gas exchange and continuously shaken at low speed on a reciprocal shaker (Eberbach, Ann Arbor, MI, USA). WEOC was determined at the beginning of the incubation, and again at the end of seven days to determine the C respired through microbial processing. This C represents the most labile C fraction of DOC and an estimate of the C respired by the stream during transport of the soil.

In order to determine the total bioavailability of C, the soils were also incubated. For soil incubations, dried and sieved soils were rewetted to 70% of field capacity (Dijkstra et al., 2007), which was determined based on soil texture (measured with a Beckman Coulter LS 230 particle size analyzer (Brea, CA, USA), using the Soil-Plant-Air-Water (SPAW) computer model (Saxton et al., 2006). Approximately 20 g of soil samples were placed in quart sized canning jars with a septum in each lid in the Adair Lab (UVM) at 21 degrees. Seven mL gas samples were taken through the septum by syringe. CO<sub>2</sub> produced by soil samples in closed jars was measured over a 24 hour period, using a LICOR 8100A Analyzer (Lincoln, NE, USA), seventeen times over the course of 81 days.

Data from the LICOR measurements from the incubations was processed using R statistical software (R Core Team, Vienna, Austria) and C production was calculated using the methods of Dijkstra et al. (2005). The area under each curve was determined in R, using integration to determine the total amount of CO<sub>2</sub> present in each jar. The difference between initial CO<sub>2</sub> levels and CO<sub>2</sub> levels at the end of the 24 hour period was calculated to determine CO<sub>2</sub> produced, which was plotted over time to calculate the short term, bioavailable, C pool.

### **3.2.6 Statistical Analyses**

JMP (SAS, Cary, NC, USA) was used for analysis of variance (ANOVA) to identify significant differences in all C and nitrogen characteristics by land cover classes. ANOVA tests were also performed to compare the data from incubations for different land covers. Linear regression was used to determine relationships between C

characteristics, nitrogen characteristics, and anions. Multiple linear regression was used to develop an equation to test the predictive power of land cover on WEOC.

The results of the fluorescence spectroscopy were analyzed using a parallel factor analysis (PARAFAC) in MATLAB to “deconvolute” the spectra into four unique components, representative of different groups of fluorescing DOM, following the protocol and quality control described by Stedmon and Bro (2008). The loadings for each component found were: C1: Ex 240-450 nm, Em 315-506 nm; C2L Ex 240-390 nm, Em 3212-459 nm; C3: Ex 264-594nm, Em 433-619 nm; C4: Ex 240-342, Em 276-433 nm (Fig 3.2). Once validated, the emission and excitation signatures of the components were compared to published values (Table 3.1) identifying C1 as terrestrial humic-like, C2 as microbial humic-like, C3 as humic-like, and C4 as protein-like.

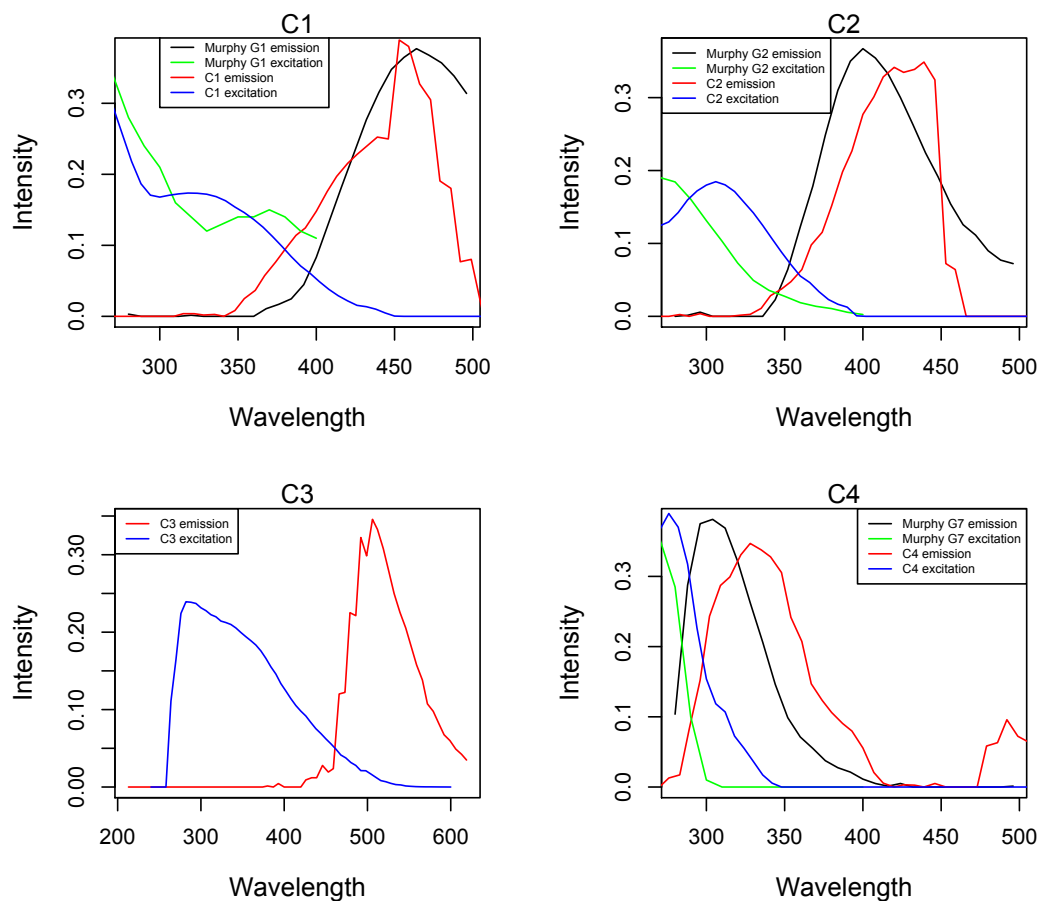


Figure 3.2. Excitation and emission loadings of the four components from the PARAFAC model, compared to loadings from Murphy et al. 2011. C1 and C2 from this study are similar to their G-1 and G2, respectively. C3 from this study has no equivalent and C4 from this study is red-shifted relative to their G7.

Table 3.1. PARAFAC component comparison and identification.

Component	Literature Components	Designation
C1 Terrestrial humic-like	Murphy et al. 2011 G1	Terrestrial humic
	Fellman et al. 2010 UVC humic-like	High-molecular-weight humic, widespread, but highest in wetlands and forested environments
	Ohno et al. 2009 C1	Reduced quinone, humic
C2 Microbial humic-like	Murphy et al. 2011 G2	Microbial humic
	Fellman et al. 2010 UVA humic-like	Low molecular weight, common in marine environments associated with biological activity but can be found in wastewater, wetland, and agricultural environments
	Ohno et al. 2009 C3	Oxidized quinone
	Yamashita et al. 2010 C3	Microbial humic
	Santin et al. 2009 C3	Microbial humic
C3 Humic (reduced)	Ohno et al. 2009 C2	Reduced quinone, humic
	Fellman et al. 2010 Humic- like	Reduced, humic-like, correlated with % anomeric, acetal and ketal
	Cory and McKnight 2005 SQ1	Reduced quinone like, plant-derived, positively related to the aromatic C content
	Yamashita et al. 2010 C2	Humic
C4 Tyrosine-like	Murphy et al. 2011 G7	Tyrosine
	Yamashita et al. 2010 C3	Protein
	Fellman et al. 2010 Tryptophan- like	Amino acids, free or bound in proteins, fluorescence resembles free tryptophan,



### 3.3 Results

#### 3.3.1 TOC and WEOC By Land Cover

Neither the amount of TOC in the soil nor the amount of WEOC in the soil varies with depth (Fig 3.3) (Appendix 2).

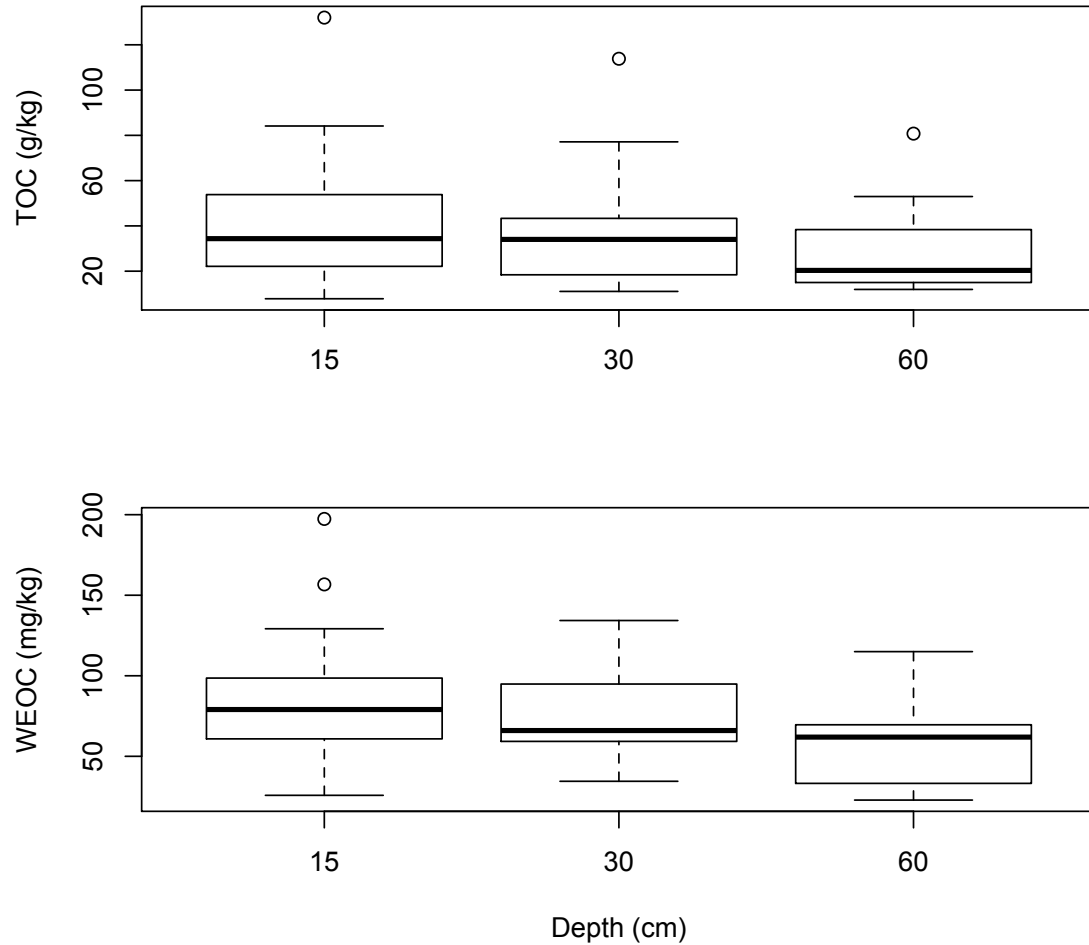


Figure 3.3. TOC and WEOC of the soils by sampling depth.

Overall, TOC variability is greater in agricultural than forested samples. TOC in agricultural land covers ranges from 11.1 to 132.0 g/kg, while TOC in forested land covers ranges from 7.8 to 53.8 g/kg.

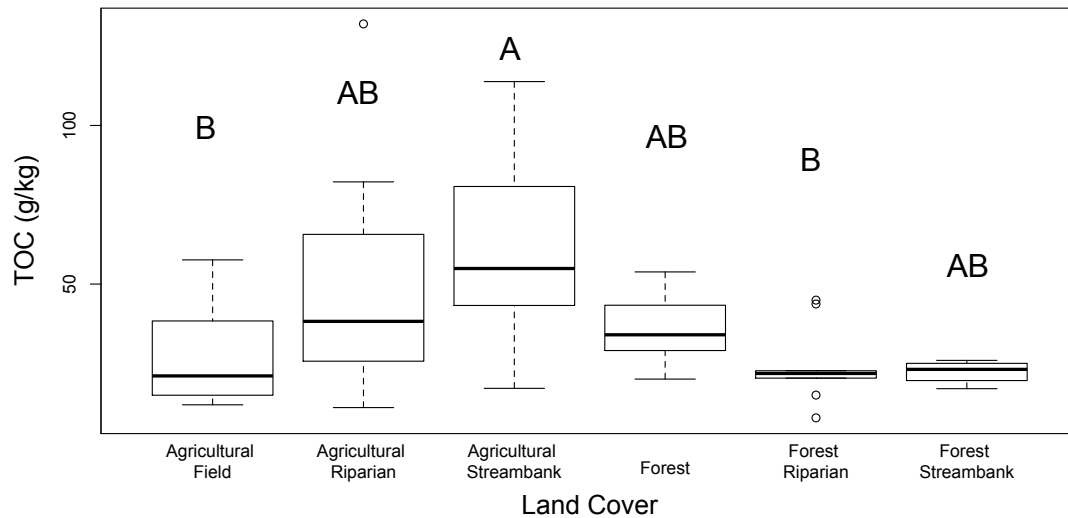


Fig. 3.4 TOC by land cover (n = 71). Boxplots show median and upper and lower quartiles in the box and range as extended lines. Land covers with different letters denote pairs of means that are significantly different ( $p < 0.05$ ).

WEOC (Fig. 3.5) and WEON (Fig. 3.6) show similar trends with overall higher concentrations in extracts from agricultural samples. WEOC in agricultural land covers ranges from 22.8 to 156.7 mg/kg, while WEOC in forested land covers ranges from 22.8 to 197.4 mg/kg. Compared to values of TOC, WEOC in samples from forested land covers show greater variability. Because the amount of WEOC in a soil varies by land cover, the WEOC in a soil sample can also be predicted using land cover with the following equation ( $p < 0.05$  for each factor):

$$WEOC \left( \frac{mg}{kg} \right) = 79.48 - 21.76(Agricultural\ Field) + 19.55(Agricultural\ Riparian) + 23.27(Forest)$$

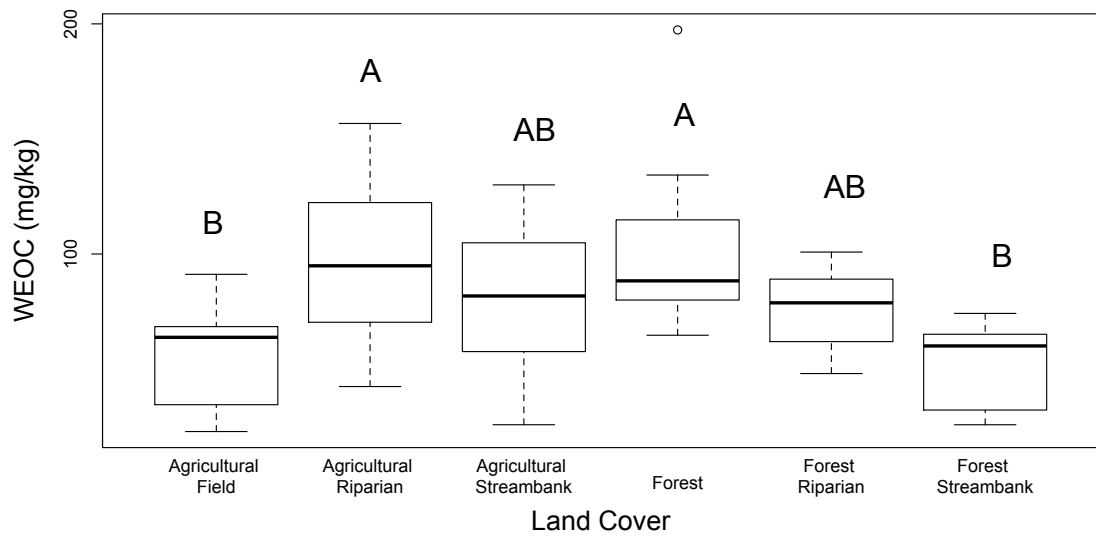


Fig 3.5 WEOC by land cover (n = 71). Boxplots show median and upper and lower quartiles in box, range as extended lines. Land covers with different letters denote pairs of means that are significantly different ( $p < 0.05$ ).

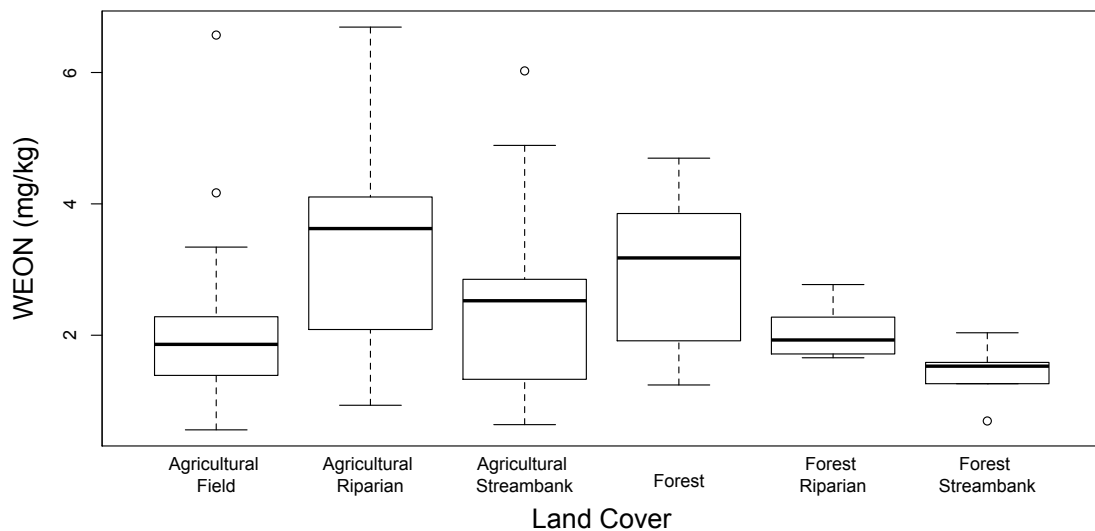


Figure 3.6. WEON by land cover (n = 71). Boxplots show median and upper and lower quartiles in box, range as extended lines. No land covers have significantly different WEON ( $p > 0.05$ ).

C:N ratios range from 8.4 to 18 and are significantly higher in the agricultural stream bank and forest stream bank land covers.

### **3.3.2 Spectral Indices and PARAFAC Components**

The spectral indices  $SUVA_{254}$ , HIX, and FI, differ significantly between samples from different land covers (Table 3.2). The agricultural stream bank HIX was significantly lower than that of the agricultural riparian, agricultural field, and forest land covers ( $p < 0.05$ ). FI is higher in the forest than in the agricultural field and agricultural riparian land covers ( $p < 0.05$ ), while the agricultural field also FI is also lower than the forest land cover ( $p < 0.05$ ).  $SUVA_{254}$  is lower in the forest land cover than in the agricultural stream bank, agricultural field, and forest stream bank land covers ( $p < 0.05$ ). PARAFAC components C1 (terrestrial humic-like) was high in extracts from forest land cover samples, but low in the forest stream bank. Component 2 (microbial humic-like) was high in extracts from agricultural field and forest stream bank. Components C3 (terrestrial humic-like) was highly variable in extracts from agricultural riparian samples, and low in forest stream bank extracts. Component 4 (tyrosine-like) was highly variable in agricultural stream bank WEOM.

WEOC is strongly negatively correlated with  $SUVA_{254}$ , and moderately positively correlated with both terrestrial humic-like PARAFAC (C1 and C3). WEOC is weakly positively correlated with HIX and PARAFAC components C2 and C4 (Fig. 3.7).

Table 3.2. Mean and standard deviation of PARAFAC components and spectral indices by land cover.

Land Cover	C1(%)	C2(%)	C3(%)	C4(%)	FI	HIX	SUVA <sub>254</sub> (L/mg m)
Agricultural Field	31 ± 3	39 ± 2	10 ± 1	20 ± 3	1.53 ± 0.17	2.91 ± 0.71	8.19 ± 4.22
Agricultural Riparian	32 ± 2	37 ± 2	11 ± 1	20 ± 4	1.49 ± 0.10	2.99 ± 0.79	6.35 ± 2.51
Agricultural Stream Bank	30 ± 3	37 ± 2	10 ± 1	24 ± 3	1.63 ± 0.14	2.26 ± 0.56	8.95 ± 4.65
Forest	34 ± 1	37 ± 1	11 ± 0.6	19 ± 2	1.69 ± 0.14	2.87 ± 0.34	4.57 ± 1.36
Forest Riparian	33 ± 2	36 ± 2	11 ± 0.6	20 ± 2	1.62 ± 0.14	2.68 ± 0.45	5.87 ± 1.34
Forest Stream Bank	30 ± 3	38 ± 2	11 ± 0.9	21 ± 4	1.55 ± 0.15	2.42 ± 0.50	9.51 ± 5.01

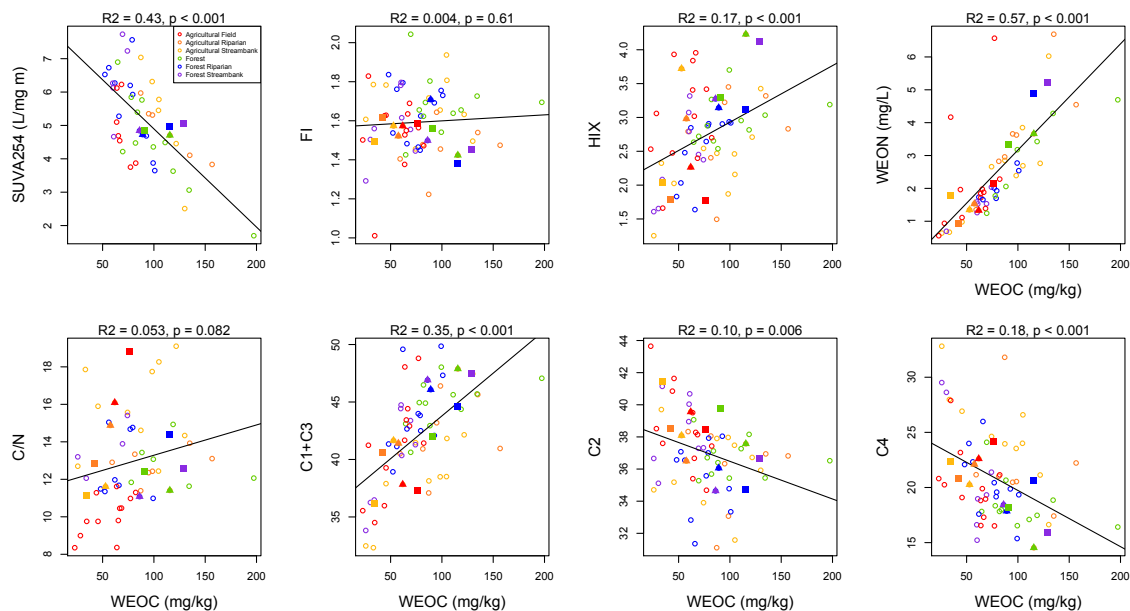


Figure 3.7. Correlation between carbon characteristics and WEOC of aqueous soil extracts. Squares represent samples for which the aqueous extract was incubated and triangles represent soils for which both the aqueous extract and the soil were incubated.

PARAFAC components co-vary with the spectral indices (Fig. 3.8). For example, the two terrestrial humic-like components (C1 and C3) show a strong negative correlation with  $SUVA_{254}$  and a strong positive correlation with HIX. C2 is weakly and positively correlated with  $SUVA_{254}$ , while C4 is positively correlated with  $SUVA_{254}$  and negatively correlated with HIX.

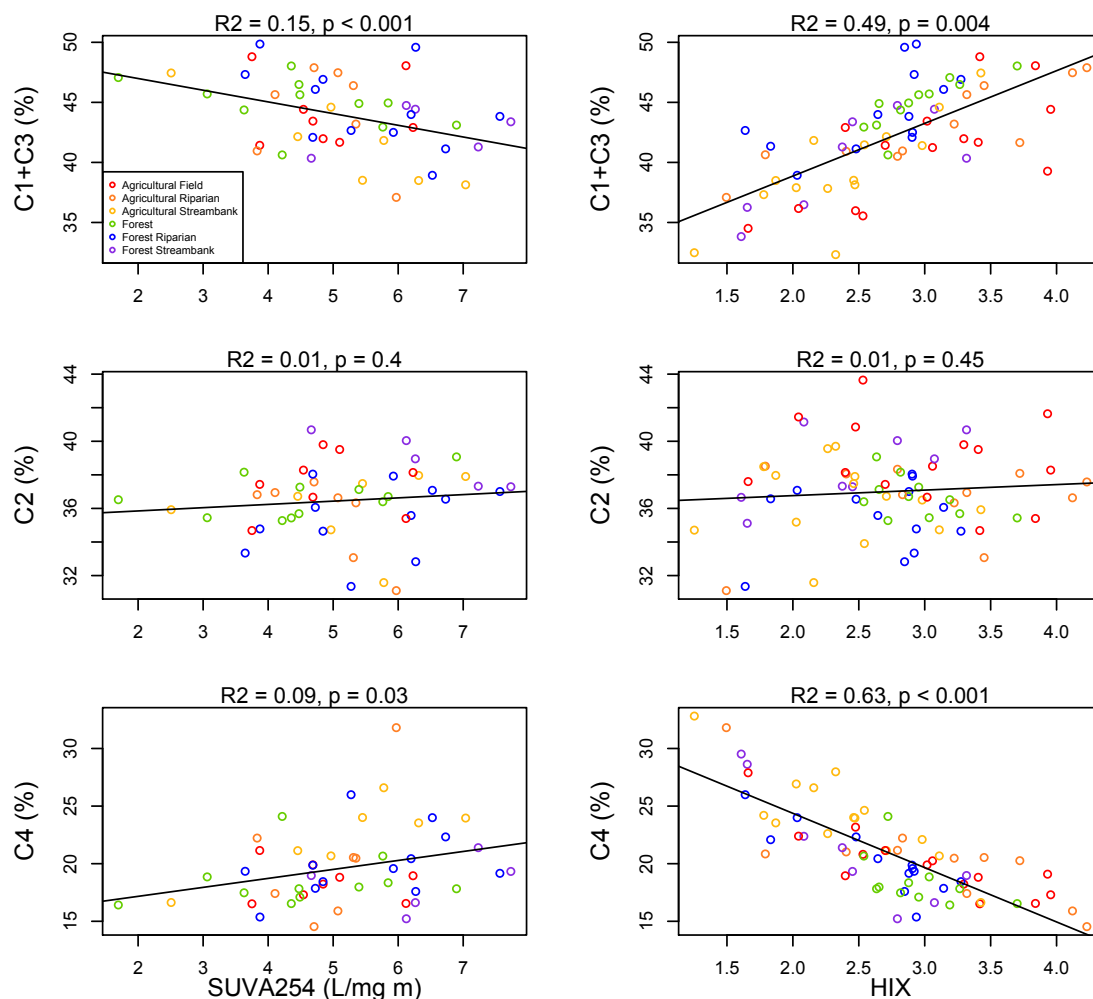


Figure 3.8. PARAFAC components regression with SUVA<sub>254</sub> (aromaticity) and HIX (degree of humification).

### 3.3.3 Incubations

ASE bioavailable C content ranged from 6.5 to 66.6% of total WEOC. In extracts from agricultural land covers, bioavailable C in the soil down to 60 cm was much lower than the in the top 15 cm of the soil column. Bioavailability is high and less variable for all depths in the forest land covers (Table 3.3, 3.4).



Table 3.3. Bioavailability of WEOC (aqueous extracts) and TOC (dried soil) of the composite soil samples from the top 15 cm of the soil column.

Land Cover	Aqueous Extract		Dried Soil	
	Bioavailable C (mg/kg)	Bioavailable C (%)	Bioavailable C (mg/kg)	Bioavailable C (%)
Agricultural Stream Bank	58.12 ± 1.00	66.61 ± 3.57	937.86 ± 105.94	2.73 ± 0.31
Agricultural Riparian	66.57 ± 3.16	48.59 ± 3.10	1062.25 ± 124.07	1.96 ± 0.23
Agricultural Field	53.42 ± 5.50	54.18 ± 1.26	749.81 ± 4897	2.13 ± 0.13
Forest Stream Bank	37.56 ± 0.87	51.30 ± 0.64	448.97 ± 15.30	1.73 ± 0.06
Forest Riparian	40.37 ± 3.19	54.00 ± 1.59	501.92 ± 82.13	2.30 ± 0.38
Forest	74.59 ± 4.18	63.46 ± 0.66	911.53 ± 175.01	2.36 ± 0.45

Table 3.4. Bioavailability of WEOC from composite soil samples from the top 60 cm of the soil column.

Land Cover	Bioavailable C (mg/kg)	Bioavailable C (%)
Agricultural Stream Bank	10.11 ± 5.12	13.73 ± 6.10
Agricultural Riparian	15.79 ± 3.10	18.97 ± 4.28
Agricultural Field	2.26 ± 11.8	6.49 ± 22.2
Forest Stream Bank	35.36 ± 2.29	51.64 ± 2.34
Forest Riparian	43.82 ± 3.01	54.36 ± 2.52
Forest	51.62 ± 1.37	59.19 ± 0.51

Some PARAFAC components are correlated with the percentage of respired C.

The terrestrial humic-like C1 has a strong positive correlation ( $R^2 = 0.60$ ) with respired C, while the tyrosine-like C4 has a weak negative correlation ( $R^2 = -0.39$ ) (Fig. 3.9).

However, there is no correlation between the amount of bioavailable C and the WEOC or TOC content (Fig. 10) or with  $SUVA_{254}$ , ( $p = 0.72$ ), FI ( $p = 0.12$ ), or HIX ( $p = 0.06$ ).

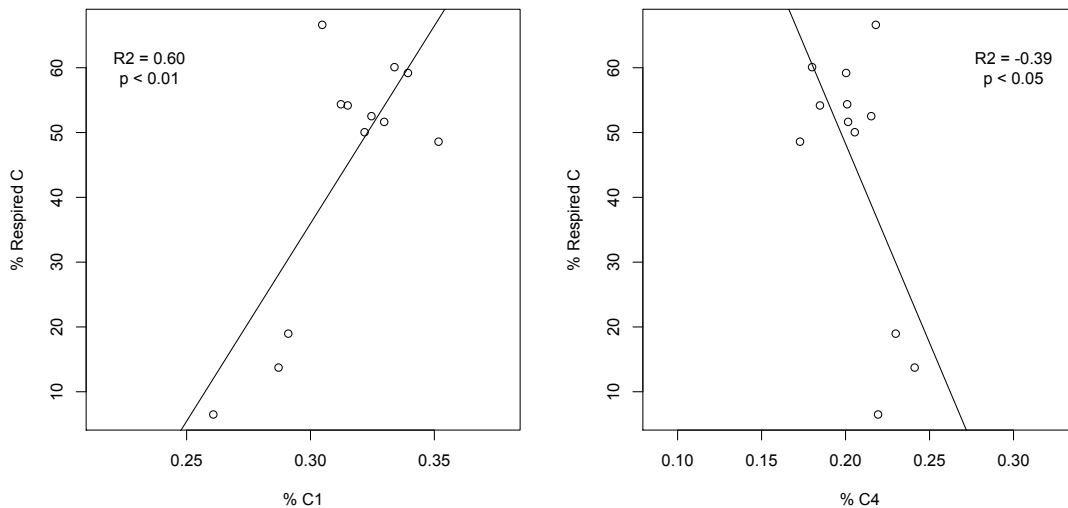


Fig. 3.9. PARAFAC components C1 and C4 vs. WEOC bioavailability, with  $R^2$  (correlation) and p-value (statistical significance) shown.

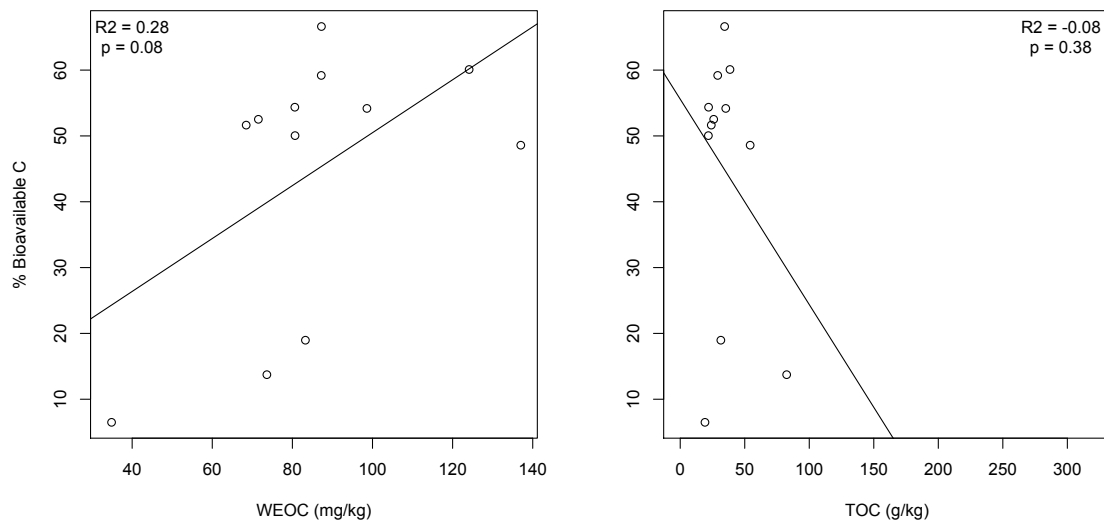


Fig. 3.10. WEOC and TOC vs. bioavailability of C in aqueous extracts, with  $R^2$  (correlation) and p-value (statistical significance) shown.

For soil incubations, bioavailability increases with TOC. The range of C respired over the first 18 days is 528 mg/kg – 1219 mg/kg (Table 3.2). Agricultural land covers have high initial C respiration and high long term C respiration, while forested land covers have lower initial and long term respiration rates. All soils respired the majority of their short term bioavailable C by day 18, maintaining low respiration for the remaining 63 days (Fig. 3.11). However, percent bioavailability of TOC is similar for all land covers, ranging from 1.7 to 2.7% (Table 3.3).

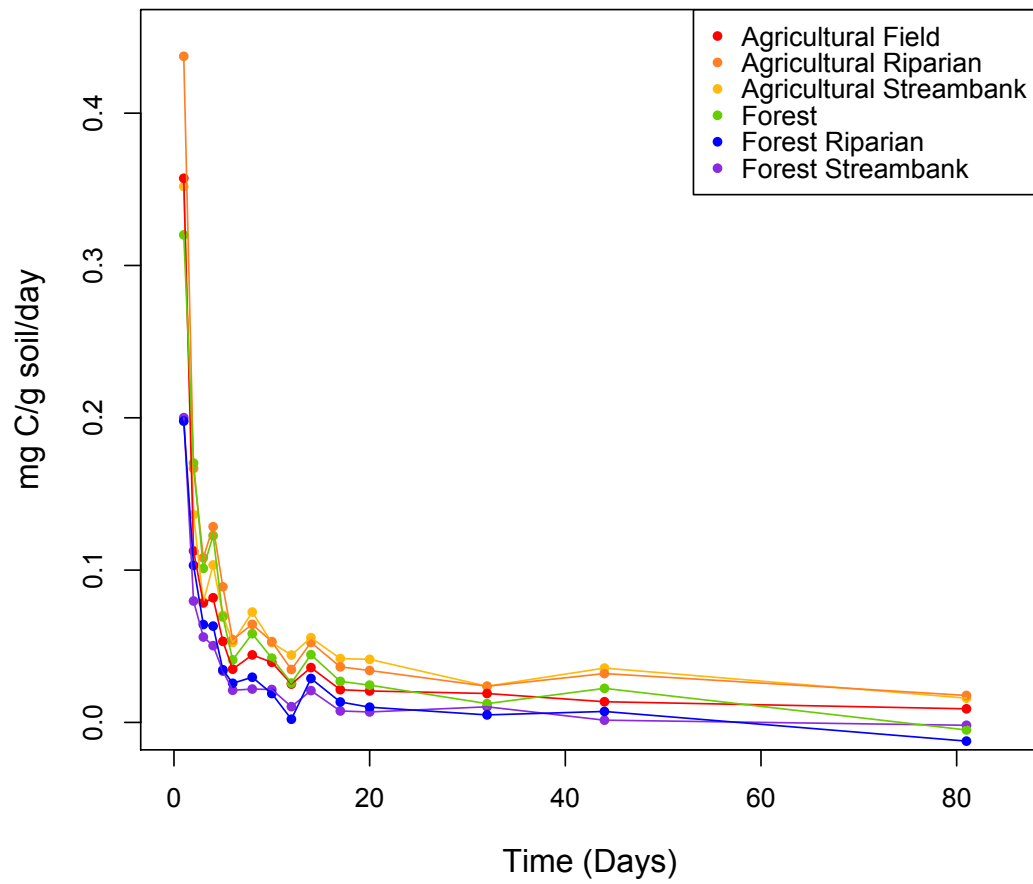


Figure 3.11. C respired from incubations of soil at 70% of field capacity over 81 days.

### **3.3.4 Temporal and Depth Variability**

The sample design allowed testing for temporal variability over the summer months (Fig. 3.12). TOC, WEOC and its characteristics showed great variation between sampling dates, explaining observed variability but the change over the course of the three month sampling period was not systematic. As the summer progressed, samples of each land cover maintained constant WEOC and PARAFAC components.

The composite soil samples that were taken during the last two sampling dates and were used for incubations have similar values of WEOC and similar proportions of PARAFAC components as the individual samples taken on the previous sampling dates.

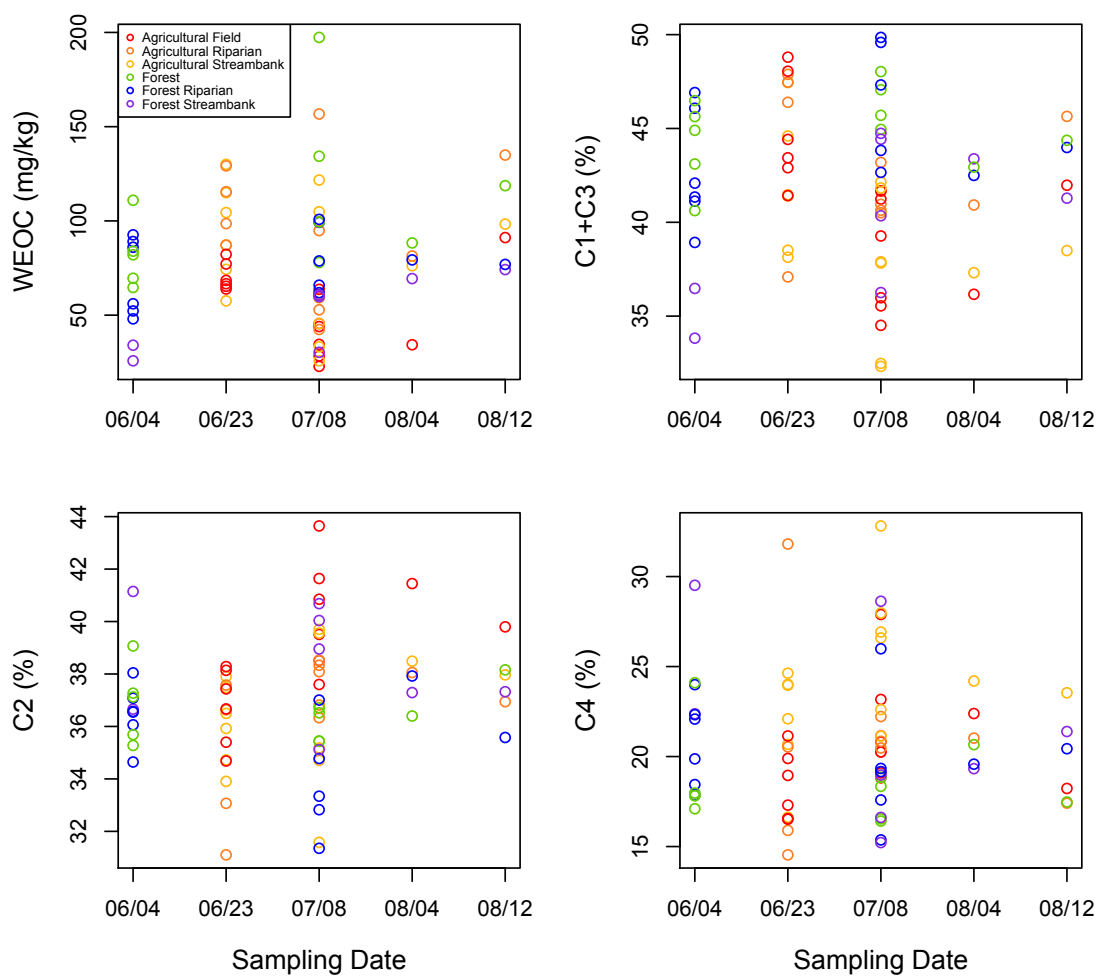


Figure 3.12. WEOC and PARAFAC components on each sampling date.

### **3.4 Discussion**

#### **3.4.1 Temporal and Depth Variability of Organic Matter**

WEOC is labile and can change over the course of several weeks due to temperature and moisture changes, mainly from precipitation (Johnson et al. 2000, Groffman et al. 2009), as well as the state of the vegetation (McLaughlin et al. 2012, Schelker et al. 2013, Dib et al. 2014). Variability within each land cover is great but no systematic changes in WEOC concentrations or optical properties are visible over the course of the three month sampling. This suggests that i) temporal variability is one important source of observed variability when combining data and that ii) this variability is not systematic, suggesting similar C processing occurs over the course of the summer. In addition, TOC and WEOC do not change systematically with sampling depth and are therefore depths integrated for statistical analyses.

#### **3.4.2 Carbon Characteristics and Processes**

Land cover has an important effect on C content in soil; for example, agricultural land uses, such as tillage and harvest, alter C in fields, while sediment deposited by the stream alters C in stream banks and riparian areas (Murty et al., 2002; Wohl et al. 2012). Results from this study indicate that even though a great variability exists in the data, the distribution of TOC, WEOC, WEON and bioavailability varies with the sampled land covers and that molecular DOM properties differ with the amount of WEOC present.

WEOC consists of the water soluble and easily leached fraction of C and belongs to the C fraction of short turnover time in soils (Boyer and Groffman, 1996; DeLuca and Keeney, 1993; Frank et al., 2012; Nelson et al, 1994). Therefore, WEOC concentrations

can vary greatly over space and time. In turn, TOC includes all pools of soil organic C, including the more recalcitrant, long turnover fractions, and is a better choice when comparing long term trends in C cycling by land cover.

The agricultural field was characterized by relatively low TOC (Fig. 3.4) and WEOC (Fig. 3.5) concentrations, which is consistent with C depletion from tillage and crop harvest (Murty et al., 2002). These agricultural practices typically homogenize soils, which should reduce the variability of soil parameters in at least the top horizons (Kalbitz et al., 2003). Agricultural vegetation results in a different quality of litter than naturally occurring vegetation (Boyer and Groffman, 1996), also capable of producing more bioavailable WEOC (Kalbitz et al., 2003). High WEOC values of the PARAFAC component C2, a component commonly found in agricultural fields, are consistent with the highly bioavailable C (Fellman et al., 2010). The percentage of bioavailable C assessed with incubations is high in the top 15 cm, but lower for the top 60 cm of the soil, indicating that the most bioavailable C is at the surface. Interestingly, WEON is low in the field and may point to leaching and runoff of N into the adjacent stream during rain events.

TOC and WEOC concentrations were high and variable in the agricultural riparian and stream bank land covers, likely due to frequent soil interactions with the river. Riparian zones represent the interface between terrestrial and aquatic systems in the RC, and are hotspots of C processing (Vidon et al., 2010). They have distinctive vegetation, and are often high in productivity (Brooks and Kyker-Snowman, 2009), leading to large C inputs. However, these areas are also influenced by river processes such as flooding, which leaches soluble C and deposits C poor sediments. Fahey et al.



(2005) also reported a high spatial variability in the C distribution and rate of C processes within riparian soils. WEOC and TOC results from this study are consistent with the high productivity and high variability in these areas. The great spatial variability and variability in C processing rates is furthermore reflected in the HIX and PARAFAC component C3 of the agricultural riparian land cover, which are equally variable, suggesting a variety of C sources and humification rates. Incubation studies showed highest values for percentage of respired C for agricultural riparian, which is consistent with the high productivity previously reported for this land cover (Sommer, 2006; Brooks and Kyker-Snowman, 2009).

Similarly to riparian areas, the agricultural stream bank is influenced by the stream (receiving sediment from or losing sediment to the stream and experiencing soil leaching) and by the proximity of the agricultural field (receiving C and nutrients from agricultural runoff.). High WEOC and TOC (Fig 3.5, 3.6) concentrations and the high variability may be explained by runoff from the agricultural field. Interactions with the stream are consistent with the low bioavailability of C, as the soluble (bioavailable) C has already been removed by the interaction with the stream. Stream bank soils also exhibit heterogeneity due to sediment deposition at unequal intervals (Jacobson et al., 2003), leading to buried horizons and a lack of uniformity in the soil. C can be stored in these buried horizons, elevating the TOC and WEOC in the soil. The stream bank soils in this study showed high variability in C4, which is protein-like, consistent with microbial C processing. The WEON accumulates in the riparian and stream bank land covers, closer to the stream, as these both have high WEON concentrations. In both the agricultural riparian and stream bank land covers, the high WEON concentration may stimulate

microbial and plant growth in the stream bank, resulting in high C production and processing.

In contrast to the agricultural land covers, the forested land covers were less variable. TOC concentrations were low in the forest land cover, WEOC concentrations were high, while both TOC and WEOC in the forest riparian and forest stream bank land covers were low. WEOC was likely high and heterogeneous in forest because of high, but variable leaf litter inputs (Batjes, 1996). However, leaf litter inputs are localized around plants, leading to heterogeneity in the amount and type of C input. High HIX values, low SUVA<sub>254</sub> values, and low C<sub>4</sub> are indicative of already highly processed, easily leached soils. While TOC may be low, due to previous leaching of these water extractable inputs, new inputs are created, causing low overall TOC, but high WEOC from the most recent inputs.

Forest riparian land cover is influenced by interactions with the stream, resulting in low TOC and low WEOC concentrations. The percentage of bioavailable C was also low in this land cover, which may be a reflection of the leaching and addition of C poor sediments from the stream. Carbon in contact with the stream has already been exposed to microorganisms, and only the most recalcitrant C remains in the soil. The PARAFAC components are similar to those from the forest land cover, but the WEOC is much lower, suggesting that C sources from both the forest and the forest stream bank are represented in this land cover.

Forest stream bank land cover experiences similar processes as the riparian land cover, resulting in low TOC and low WEOC. However, this land cover is more impacted by stream and soil water processes than the other land covers, which are driven by

terrestrial processes, as evidenced by the low C1 and C3, the terrestrial humic-like components, and high C2, the microbial humic-like component in the extracts of these soils. As water interacts with the soil in the stream bank, WEOC is removed by the stream and (Hupp et al., 2015). Similarly, sediments deposited by the stream have already been exposed to leaching and stream processes while in the river. Carbon is leached from the soil by stream water, resulting in low C, while stream sediments, which have experienced microbial processing in the stream, are deposited, resulting in high C2 (Hupp et al., 2015) and high bioavailability.

Despite the differences in TOC, WEOC, and WEON, all parts of the RC share certain C characteristics. For example, while values of the fluorescence index (FI, an indicator of DOM provenance) showed variation samples by land cover, average values ranged from 1.5 to 1.7, indicating WEOC in all land covers is mostly terrestrial with microbial influence. (McKnight et al., 2001). Ratios of C and N (C:N), another measure of terrestrial vs. microbial DOM, is so variable (ranging between 8 and 18) that differences between land covers are not significant. This range encompasses both terrestrial (high C:N) and aquatic (low C:N) sources (Muller and Mathesius, 1999), suggesting a mix of sources.

In addition, several C characteristics are dependent on the amount of C, independent of the land cover the soil came from. High values of WEOC in an extract are associated with an increase in the terrestrial humic-like component, while low values are associated with the tryptophan-like component C-4. In addition, extracts with higher values of WEOC tend to be less aromatic and more humified than lower values. This

supports the idea that the source material is similar throughout the RC. Increased C in certain land covers is coming from a humified, mainly terrestrial C pool.

### **3.4.3 Bioavailability Using Spectral Methods: A Valid Approach for Soils?**

Incubation studies in which C cycling is measured either as decrease of reactant (e.g. DOC) or increase in product (e.g. CO<sub>2</sub>) are a direct measure of C bioavailability. However, because incubations are laborious, other metrics, especially PARAFAC components derived from fluorescence EEMs have been increasingly used (Stedmon et al., 2003; Cory and McKnight, 2005; Stedmon and Markager, 2005; Murphy et al., 2006; Ohno et al., 2009; Fellman et al., 2010; Yamashita et al., 2010).

Several studies have found significant correlation between their microbial humic-like component (C2 in this study) and biological activity, and the presence of components with similar loadings are used as an indicator for DOM bioavailability by many authors (Stedmon et al., 2003; Cory and McKnight, 2005; Stedmon and Markager, 2005; Murphy et al., 2006).

Both C1 and C3 are consistent with terrestrial humic-like material and correlate positively with indicators for humified (HIX), but negatively with SUVA<sub>254</sub>, indicating low aromaticity. C4 contains aromatic WEOC (positive correlation with SUVA<sub>254</sub>) and the negative correlation between C4 with HIX is consistent with mostly protein related OM (which can be aromatic as indicated by the SUVA<sub>254</sub> values) (Fig. 3.8).

Comparing PARAFAC components from this study to the direct measure of bioavailability via accompanying incubation results, no significant correlation between C2 and bioavailability could be found. However, C1 is positively correlated with bioavailability and C4 is negatively correlated with bioavailability (Fig. 3.10). The

association between a protein-like component and aqueous bioavailability is similar to the results of Baker et al. (2004), who found a correlation between tyrosine and bioavailability.

The correlation between a terrestrial humic-like component, rather than a microbial humic-like component with bioavailability may be influenced by the fact that the soil extracts are target terrestrial OM, as evidenced by the FI values. Stream water DOM, which was measured in the previously mentioned studies, may have a stronger microbial signature as terrestrially sourced DOM is transformed into microbially sourced DOM due to microbial processing in the stream. Therefore, the source of the DOM and the extraction procedure of the DOM must be accounted for in assessing bioavailability based on spectral proxies.

These results indicate that the interpretation of bioavailability based on PARAFAC components might be dependent on the type of substrate used and may vary. In this study, not all PARAFAC components are a reliable indicator for DOC bioavailability.

#### **3.4.4 The Relationship Between SOC, WEOC, and Bioavailable C**

WEOC and TOC are not correlated with bioavailable WEOC (Fig. 3.11); the variability in the bioavailability is too great to make predictions based C content. Therefore, the amount of C in a soil or in an extract is not indicative of the potentially bioavailable C that may be released to a stream. Neither SOC nor WEOC can be used to predict the bioavailability of C in a sample, as the different types of OM in a soil are more important than the amount of C in determining bioavailability than the amount of C.

### **3.5 Conclusions**

The SOC in a soil and the potential DOC leached from the soil do differ between the land covers sampled, supporting the first hypothesis. These differences in C do have a molecularly driven component, supporting the second hypothesis, with differences in the fluorescence properties of the DOM, suggesting that the C heterogeneity is driven on the molecular scale. However, the amount of C, not the land cover, may be the driving force behind these differences. The bioavailability of the C cannot be predicted by land cover or by spectral methods. Overall, in the Mad River corridor, land cover and land use is a driving factor in the type and amount of C stored in soils, but not the bioavailability. Further research may be pursued to use spatially distributed data to generate GIS layers of WEOC amount and type throughout the RC.

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## **CHAPTER 4: THE EFFECT OF SOIL STORAGE AND AQUEOUS EXTRACTION METHODS ON WATER EXTRACTABLE CARBON (WEOC) CHARACTERISTICS**

### **Abstract**

The laboratory methods used in the processing, storage, and extraction of soils greatly influence the amount and type of dissolved organic matter (DOM) extracted. This causes difficulty in comparisons between studies and in the application of the data to better understand natural processes. Aqueous soil extracts (ASE) are typically prepared to represent soil solution, however methods vary introducing uncertainty when comparing results. The objective of this study was therefore to test laboratory methods and their effect on water extractable organic carbon (WEOC), fluorescence properties, and bioavailability, including the effect of soil drying, soil storage, and the choice of extraction solution. For this, ASE were prepared from soils that were field moist, dried, and dried and stored for two years. In addition, dried soils were extracted using different solutions including a salt solution, river water, and double deionized (DDI) water. Results indicated WEOC concentration and microbial humic-like fluorescence from extracts of dried soils were higher than those in extracts of field moist soils, while WEOC concentration and microbial humic-like fluorescence was highest in extracts of soils stored long term. In addition, the bioavailability of WEOC was higher in dried soils than field moist soils. The extraction solutions of DDI water and river water produced DOM with similar fluorescence properties, while the salt solution extracted a different pool of carbon (C). Overall, the effects of drying the soils need to be considered when assessing DOM and DI water extracts produced WEOC of similar fluorescence properties as river water.

## 4.1 Introduction

Soils are an important terrestrial carbon (C) sink and a great amount of research is devoted to improving understanding of soil C and organic matter (OM) dynamics (Bartlett and James, 1980; Davidson et al., 1987; McCarty and Bremmer, 1993; Ludwig et al., 1999; Haynes, 2000; Kaiser et al., 2001; Jones and Willet, 2006; Perdrial et al., 2012). In many cases, soil solutions are studied *in situ* and soil solution is sampled without major disruption of the soil fabric using *in-situ* approaches (e.g. suction cups, or passive tension and zero-tension samplers, Weihermueller et al., 2007; Perdrial et al., 2012). When *in situ* soil solution extraction is difficult (or when other soil characteristics are of interest) soil can be sampled and subjected to further analysis in the laboratory to assess physical (e.g. bulk density), chemical (e.g. carbon content), or biological (e.g. microbial community structure) characteristics (Bartlett and James, 1980; Haynes and Swift, 1990). Leaching of soils with aqueous solutions (aqueous soil extracts or ASE) is a common practice to obtain an analogue for soil solution from soils in the laboratory, however, soils are typically processed following specific protocols and/or stored for extended periods of time.

For example, to limit microbial processes, soil samples are often dried (Bartlett and James, 1980; Davidson et al., 1987; McCarty and Bremmer, 1993; Ludwig et al., 1999; Haynes, 2000; Kaiser et al., 2001; Jones and Willet, 2006) and sieved to exclude fine roots and rocks. Such samples can then be archived and stored for a long time before analysis (Bartlett and James, 1980; Walworth, 1992; Kaiser et al., 2015), however, several studies have shown that these procedures variably alter soil characteristics and composition of soil leachate. For example, air drying leads to disruption of soil

aggregates that otherwise protect C from being leached out (Bartlett and James, 1980; Haynes and Swift, 1990; Kaiser et al., 2015). Previous work has shown that drying affects the most unstable soil aggregates that are broken up during subsequent sieving, thus exposing previously protected organic matter (Haynes and Swift, 1990). Several studies have aimed to quantify the effect of air drying indicating 2 to 10 times increase in dissolved organic carbon (DOC) extraction compared to soils processed field moist (Davidson et al., 1987; McCarty and Bremner, 1993; Ludwig et al., 1999; Haynes, 2000; Kaiser et al., 2001; Jones and Willet, 2006).

In addition to the physical disruption of aggregates, chemical changes can occur in the C due to long term storage and drying, resulting in changes to the water extractable organic C (WEOC) pool. Drying of soil greatly increases the organic carbon and nitrogen released upon rewetting (Kaiser et al., 2015; Bartlett and James, 1980). Zsolnay et al. (1999) used fluorescence spectroscopy to quantify the chemical changes in the soil occurring during air drying. They found the increased dissolved organic matter (DOM) released in the aqueous extraction of air dried soils correlated with an increase in more humified DOM, suggesting the air drying process makes this less bioavailable, humified organic matter more available to microorganisms. Storage time of dried soil can also alter both the physical and chemical characteristics (Bartlett and James 1980), as some microbial activity can continue in dried soils (van Gestel et al. 1991).

The laboratory methods used in the processing, storage, and extraction of the soils can also greatly influence the amount and type of DOM extracted, causing difficulty in comparisons between studies and in the application of the data to better understand natural processes. ASE represent an important source of information on soil solution and

are routinely prepared in many laboratories (Davidson et al., 1987; McCarty and Bremner, 1993; Ludwig et al., 1999; Haynes, 2000; Kaiser et al., 2001; Jones and Willet, 2006). The preparation of ASE can vary in the choice of extraction solution (Gabor et al., 2015), soil to liquid ratio and shaking time (Haynes and Swift, 1990) and all of these choices can impact the composition and characteristics of the extract. For example recent research showed that leached DOM fractions strongly depend on the extraction solution (McDowell et al., 2006; Gabor et al., 2015):  $\text{CaCl}_2$  based extracts showed a stronger microbial signature than water based extracts.

ASE can sometimes be the only way of gaining information on soil solution even though it is unlikely that ASE fully represent mobile soil solution (Perdrial et al., 2012). The concentration of DOM in an extract, affected by the initial ratio of soil to water, also affects the structure and behavior of DOM (Ghosh and Schnitzer, 1980), and increased concentration may lead to the formation of aggregates. The pH of the extract, influenced by the soil itself, may also affect the behavior of DOM, and induce artifacts, especially in comparing agricultural to stream systems (Zsolnay, 2003). When DOM is separated from the particulate using filtration the choice of filters can further impact DOM (Zsolnay, 2003).

In chapter 4 of this work, ASE is used to represent stream water composition after considerable stream bank failure and soil flushing. The objective of this study is to determine whether there is a quantifiable relationship between ASE soil treatments. Field moist and air dried recently collected soils, and long term stored soils are extracted and compared, as well as different extract solutions. It is hypothesized that dried soils release higher amounts of C upon water extraction than field moist soils, and that the long term



storage of soils also increases the amount of C extracted. These comparisons can be used to better understand and interpret results from studies using ASE of air dried soil, such as in chapter 4.

## **4.2 Materials and Methods**

### **4.2.1 Field Sampling**

In order to compare the effect of soil storage time and drying on WEOC composition, long term dried and stored soils (hereafter referred to as archived), freshly collected and air dried (referred to as dried), and freshly collected field moist soil samples (referred to as moist) were used in this study. Archived samples were obtained from the Ross lab in the department of Plant and Soil Science at UVM. These soils had been collected as part of the EPSCoR Research Adaptation to Climate Change (RACC) project over several campaigns in the summer 2013 on several land covers. Samples were taken in eight transects, with a sample each in the stream bank, riparian buffer, and far stream (forest or agricultural field) areas. Samples were homogenized, air dried, and sieved to 2 mm prior to storage. After 2 years of storage, 71 samples of archived soil from surface horizons (0–15 cm) were selected, extracted and analyzed to allow the selection of representative samples from agricultural and forested land covers (Fig. 4.1). Based on this initial analysis two sites were selected and samples were subjected to further analysis.

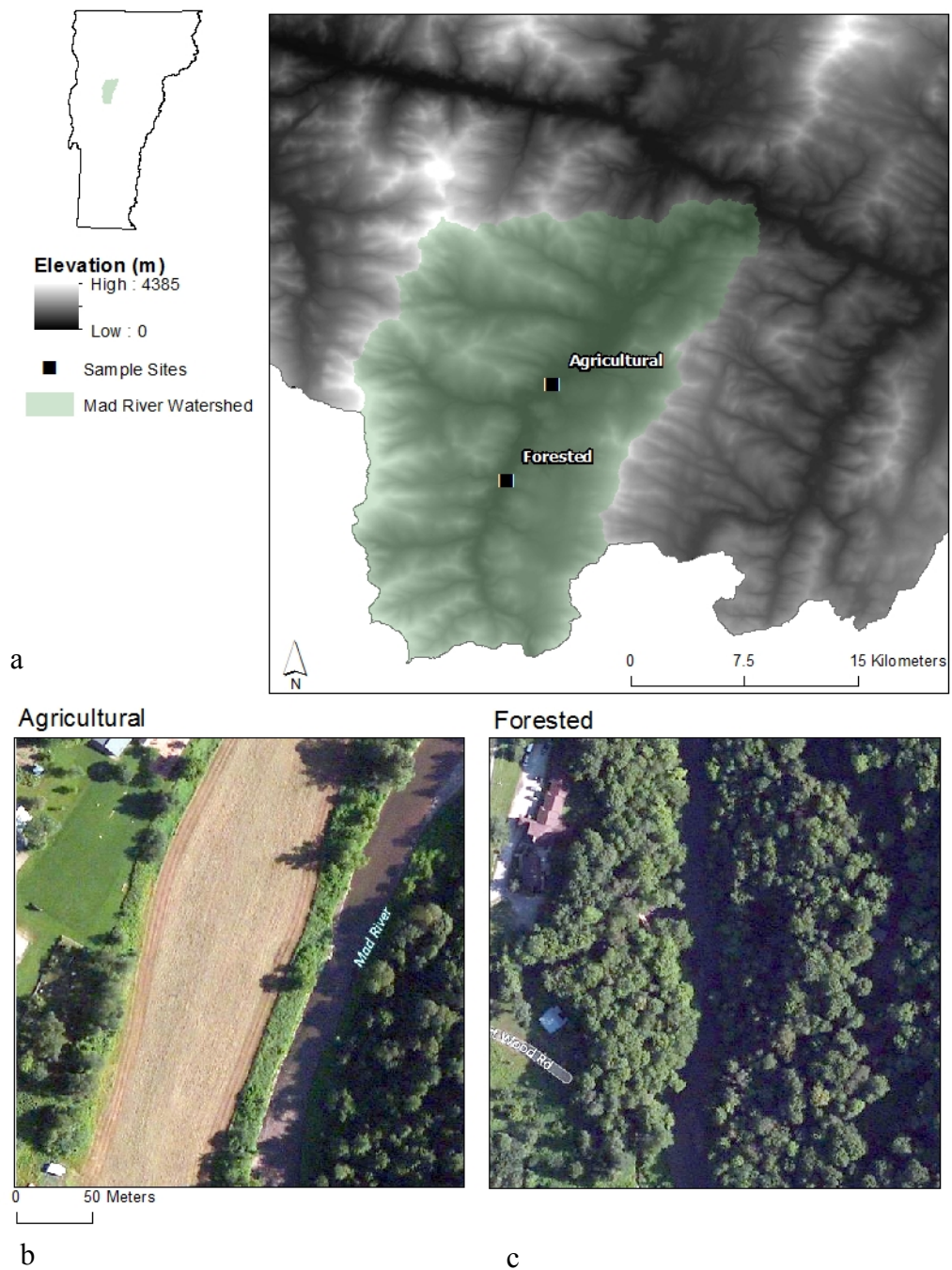


Figure 4.1. (a) Location of the Mad River watershed in the Winooski watershed in northern Vermont. (b) The agricultural site is located close to Waitsfield Elementary. (c) The forested site is located close to Riverside Park.

These two sites were resampled during the summer of 2015. Soil samples were collected on June 4 and 23 and July 8, 2015 at each site, in two transects following the sampling scheme already employed in 2013. Samples were taken from the stream bank, the riparian area, and 10 m into the far stream area (field or forest) and three depths (0-15 cm, 15-30 cm, and 30-60 cm or refusal). After the initial sample collection, additional samples were taken as composite samples on August 4 and 12, 2015 to reduce the sample number for laboratory analyses. For this, ten samples from each land cover type were collected, combined and mixed in the lab, resulting in one homogenized sample for each land cover and sampling day.

#### **4.2.2 Laboratory Analyses**

Archived samples were used without further treatment, while newly collected samples were split and sieved field moist to 2 mm (moist) and the other set was air dried and sieved to 2mm (dry). All soils were extracted with deionized (DI) water at a solid/liquid ratio of 1:5 and shaken on a reciprocal shaker (Eberbach, Ann Arbor, MI, USA) for 1 hour, followed by centrifugation to remove the suspended particles. To assure that solid to liquid ratio was the same in all soils, the amount of soil water already present in the field moist soils was included in the calculation for solid solution ratio.

The influence of the extract solution was tested on a subset of the dried soils only, one from the forest stream bank and one from the agricultural stream bank. Each soil was extracted in the same method as previous samples, but with three difference extract solutions: DDI water, a 0.02 M calcium chloride ( $\text{CaCl}_2$ ) solution, and filtered (to 0.7  $\mu\text{m}$ ) water collected from the banks of the Winooski River in Winooski, VT at baseflow.

The extracts were analyzed using the Aqualog Fluorescence Spectrometer for organic matter characteristics.

After centrifugation, about half of the supernatant was filtered through a 0.45  $\mu\text{m}$  nylon filter (Merck Millipore Ltd., Cork, Ireland) into DI-washed glass vials for inorganic C analysis and into 15 ml metal free tubes for anion analyses. The other half of the solution was filtered through combusted 0.7  $\mu\text{m}$  combusted glass fiber filter (Whatman GF/F, Buckinghamshire, UK) into combusted amber glass vials for organic C, total nitrogen, and spectroscopic analyses of water extractable organic matter (WEOM) (Fig. 4.2).

Dissolved inorganic C (DIC), DOC, and total dissolved nitrogen (TDN) were measured using a Shimadzu Total Organic C Analyzer (Columbia, MD, USA). DOC and DIC concentrations were determined by infrared detection of  $\text{CO}_2$ , after catalytic oxidation of OC at 720 degrees C and acidification of IC, respectively. TDN was determined using catalytic thermal decomposition at 720 degrees C and chemiluminescence detection. Anions were measured using ion chromatography (IC) (Dionex, Sunnydale, CA) to determine nitrate ( $\text{NO}_3^-$ ) concentration as proxy for inorganic N. Organic nitrogen was then calculated by subtracting  $\text{NO}_3^-$ -N from TDN.

Absorbance and fluorescence spectroscopy was used to characterize WEOM using a Horiba Aqualog Fluorescence Spectrometer (Horiba, Irvine CA, USA).

Absorbance at 254 nm was also used to determine the necessary dilution factor for fluorescence analysis to reach an absorbance between 0.1 and 0.3 to reduce the inner filter effect (Ohno et al, 2002; Miller et al., 2010). Fluorescence emission was collected at range of EM 212.62-619.21 (increment of 3.336) over the excitation range of EX 240-

600 nm (increment of 3 nm) to generate excitation emission matrices (EEMs). Blanks of ultrapure water (18.2 MΩ cm<sup>-1</sup>) were measured daily and subtracted from the sample EEMS, intensities were normalized to the area under the water Raman peak at 350 nm and inner filter effects were additionally corrected based on UV absorbance data (Ohno, 2002; Miller et al., 2010).

Several indices were calculated from absorbance and fluorescence data: Filtered undiluted samples were measured to determine absorbance at 254 nm and specific UV vis absorbance (SUVA<sub>254</sub>) was calculated as the absorbance intensity at emission 254 nm normalized to WEOC (in mg/L) multiplied by 100 to account for conversions from the cell path length (1cm) to m. SUVA<sub>254</sub> is a measure of C aromaticity (Weishaar et al., 2003) and can help to identify the presence of recalcitrant C.

Fluorescence index (FI) and humification index (HIX) were calculated using Matlab R2014b. The FI provides information on DOC provenance (microbial or terrestrial) (McKnight et al., 2001; Cory and McKnight, 2005) and is used constrain sources of WEOC. FI is calculated as the intensity at emission 470 nm divided by intensity at 520 nm, each at excitation 370 nm (Cory and McKnight, 2005). The HIX is a measure of the humification (or degree of polycondensation) of DOC (Zsolnay et al., 1999; Ohno, 2002) and is calculated as the area under emission 435-380 nm divided by the area at 300-345 nm, each at excitation 254 nm.

Bioavailability of WEOC was determined on aqueous soil extracts by incubations using established methods (McDowell et al., 2006). Aqueous extracts were prepared as for analysis of WEOC, combining 50 mL of the extract with 0.5 mL of an inoculum in combusted glass flasks. The inoculum was prepared with 0.6 g total of soils from each

land cover in 74.4 mL water hand shaken for 1 minute and allowed to rest for 24 hours, after which the supernatant was removed and used as the inoculum. The inoculated extracts were then transferred into Erlenmeyer flasks, covered partially with parafilm to allow for gas exchange and continuously shaken at low speed on a reciprocal shaker (Eberbach, Ann Arbor, MI, USA). WEOC was determined at the beginning of the incubation, and again at the end of seven days to determine the C loss through microbial processing using methods outlined above. This C represents the most labile C fraction of DOC and provides estimates for DOC as a source for CO<sub>2</sub> to the atmosphere.

Total organic C (TOC), representing the total solid phase C in g/kg soil, was measured for all dried soil samples using an elemental analyzer (CE instruments NC 2500, Lancashire, UK) on dried, 2 mm sieved soils that were ground in a ball mill and 0.2 mg of each sample was transferred to tin capsules (Costech, Valencia, CA, USA) for combustion at 1800° C.

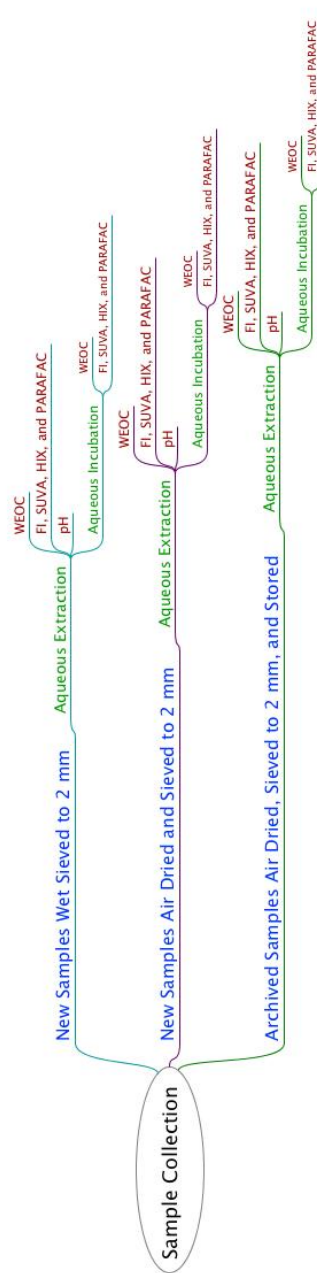


Figure 4.2. Sample splits and corresponding laboratory analyses.

### **4.2.3 Statistical Analyses**

FI, HIX, and SUVA<sub>254</sub> were calculated for the spectroscopy data, except for the comparison of extract solution, which used FI, HIX, and absorbance at 254 nm. The statistical program JMP (SAS, Cary, NC, USA) was used to perform the data analyses. ANOVA was used to compare archived, dried, and moist samples, and multiple linear regression was used to test the relationship between TOC and WEOC of moist and dried soils.

## **4.3 Results**

### **4.3.1 Soil Drying and Storage**

TOC was similarly variable for both archived and dried soils, ranging from 5 to 235 g/kg (Fig. 4.3). However, each sample treatment (archived, dried, and moist) yielded significantly different WEOC extracts ( $p < 0.5$ ) (Fig. 5.3). Aqueous extraction of dry soils resulted in higher WEOC (g/kg soil) than for moist soil, with even higher values for archived soils. WEOC in extracts of archived soils ranged from 36 to 878 mg/kg, while the dried soil extracts had a range of 23 to 197 mg/kg, and field moist extracts had from 12 to 73 mg/kg.



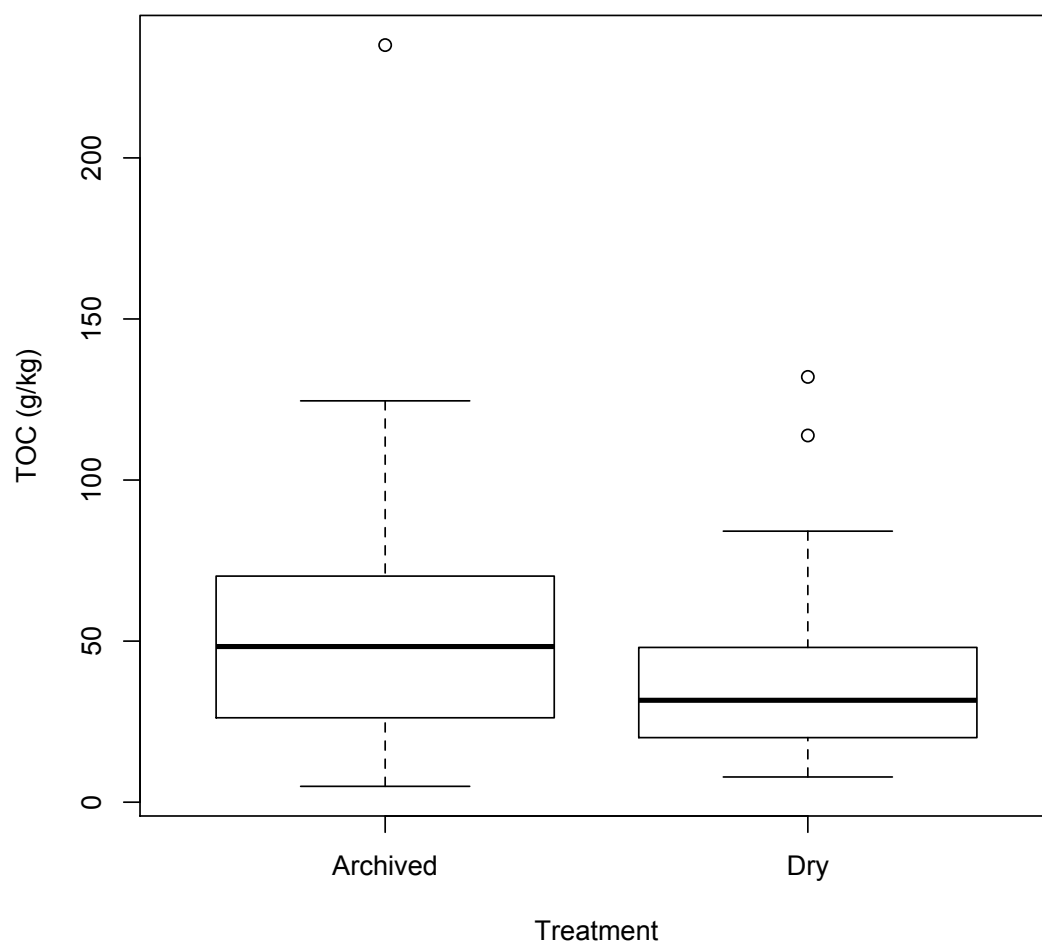


Figure 4.3. TOC comparison between archived soil and newly sampled dry soil. Boxplots show median and upper and lower quartiles in box, range as extended lines.

WEOC from dry soil extracts had a moderate positive correlation with TOC, while WEOC from moist soil extracts have no significant relationship (Fig. 4.4). However, WEOC concentration from the aqueous extraction of dried soils is highly variable compared to the concentration from the extraction of moist soils.

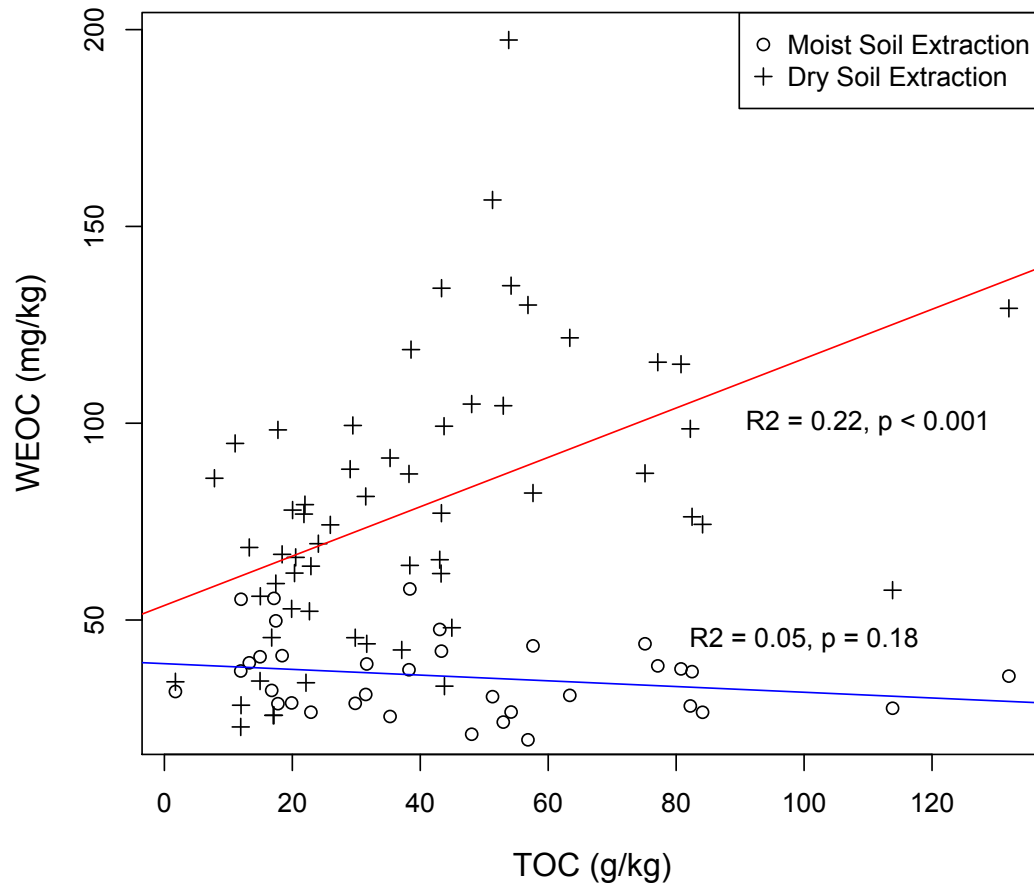


Figure 4.4. Water extractable organic C (WEOC) compared to total organic C (TOC) for aqueous extractions of dried soil (red line) and field moist soil (blue line).

PARAFAC component abundance for C2 (microbial humic-like) and C4 (protein-like) differed significantly between treatments ( $p < 0.05$ ); C2 was found highest in archived soils ( $41.5 \pm 3.0\%$ ), intermediate in dried soils ( $37.2 \pm 2.3\%$ ), and lowest in field moist soils ( $30.9 \pm 5.9\%$ ), while the opposite was true for C4, with  $16.5 \pm 4.3\%$  in extracts of the archived soil,  $20.8 \pm 3.6\%$  in the dried soil extracts, and  $35.9 \pm 7.0\%$  in the field moist soil extracts. C1 and C3 (terrestrial humic-like) together were similar in both archived and dried soils,  $42.0 \pm 3.5\%$ , and  $42.0 \pm 3.9\%$  respectively, but significantly lower ( $p < 0.05$ ) in the extracts of field moist soils at  $33.1 \pm 7.5\%$ .

HIX and  $SUVA_{254}$  were also significantly different between treatments ( $p < 0.05$ ). HIX was highest in archived soil extracts,  $3.1 \pm 0.9$ , lower in the dried soil extracts,  $2.7 \pm 0.6$ , and lowest in the field moist soil extracts,  $1.4 \pm 0.6$ .  $SUVA_{254}$  showed the opposite trend of HIX and was lowest in the extracts of the archived soils ( $4.1 \pm 4.1$  L/mg m), higher in the dried soil extracts ( $7.3 \pm 3.8$  L/mg m), and highest in the field moist soil extracts, ( $24.3 \pm 8.5$  L/mg m). FI was constant for all treatments, with a range of 0.46 to 5.67 (Fig. 4.5).

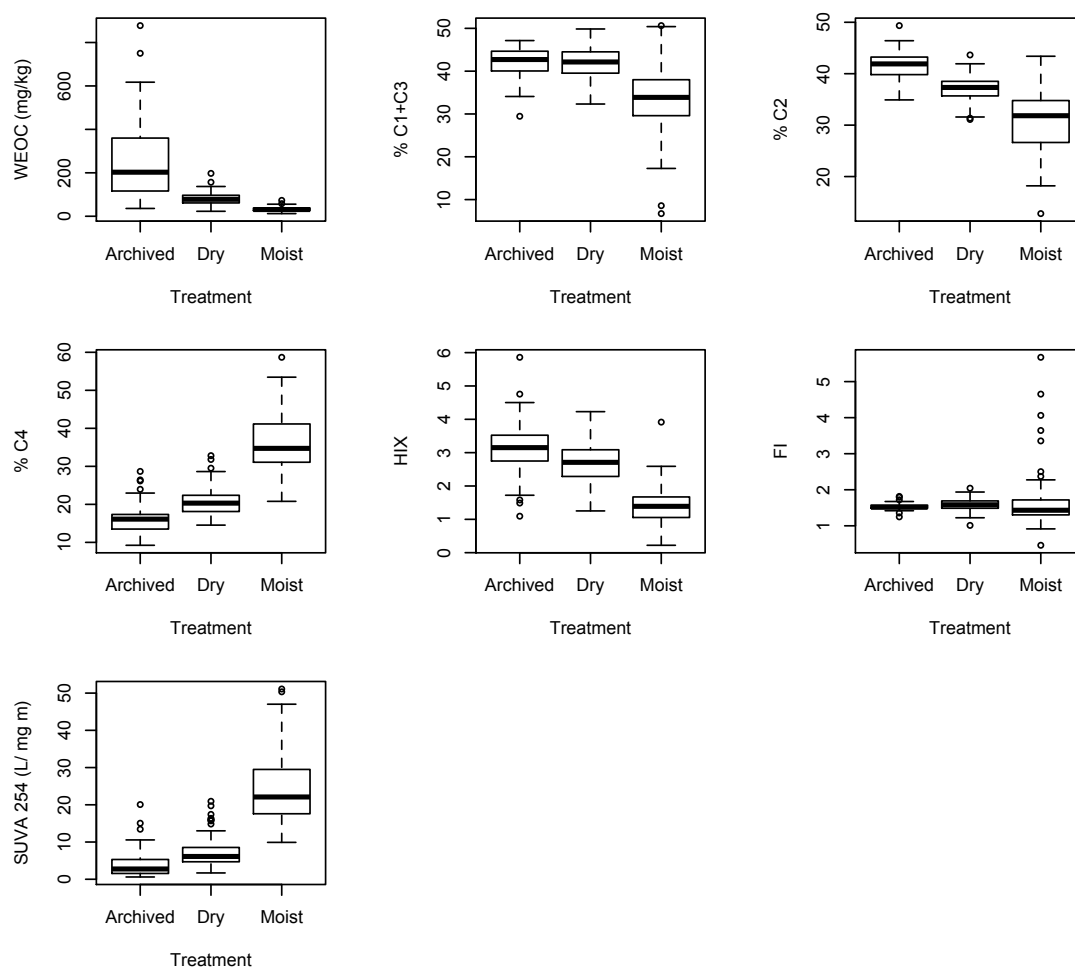


Figure 4.5. Water extractable organic C (WEOC), PARAFAC components, HIX, SUVA<sub>254</sub>, and FI comparisons between archived soil, newly sampled dry soil, and newly sampled moist soil. Boxplots show median and upper and lower quartiles in box, range as extended lines.

Respired WEOC was measured for both dried and field moist, but not for archived soils. Amount of respired C was significantly lower ( $p < 0.05$ ) for moist soil aqueous extracts, with a range of 1.1 to 50.3%, than for dry soil aqueous extracts, with a range of 6.5 to 66.6% (Fig. 4.6).

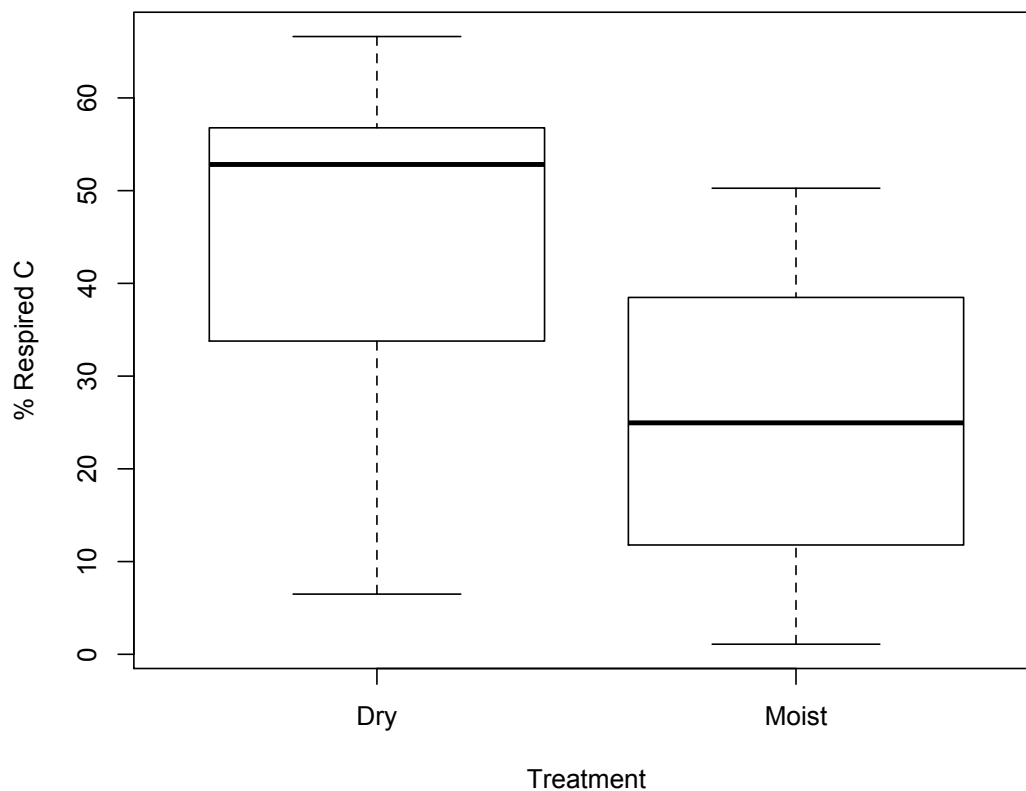


Figure 4.6. Respired C expressed as percentage of dry and moist soil. Boxplots show median and upper and lower quartiles in box, range as extended lines.

#### **4.3.2 Impact of Extract Solution Composition on WEOM Characteristics**

The impact of extraction solution was only tested on dry and moist samples (not archived). Within the selected subset of soils, WEOM extracted with the  $\text{CaCl}_2$  solution had higher FI (ranging from 1.8 to 2.1), lower HIX (from 1.9 to 3.0), and lower absorbance (from 0.14 to 0.16) compared to the other two solutions (Fig. 4.7). In contrast, extracts with DDI water had FI from 1.4 to 1.6, HIX from 3.7 to 3.9, and absorbance from 0.62 to 0.76, and Winooski River water extracts had FI from 1.6 to 1.6, HIX from 4.2 to 4.4, and absorbance from 0.3 to 0.7.

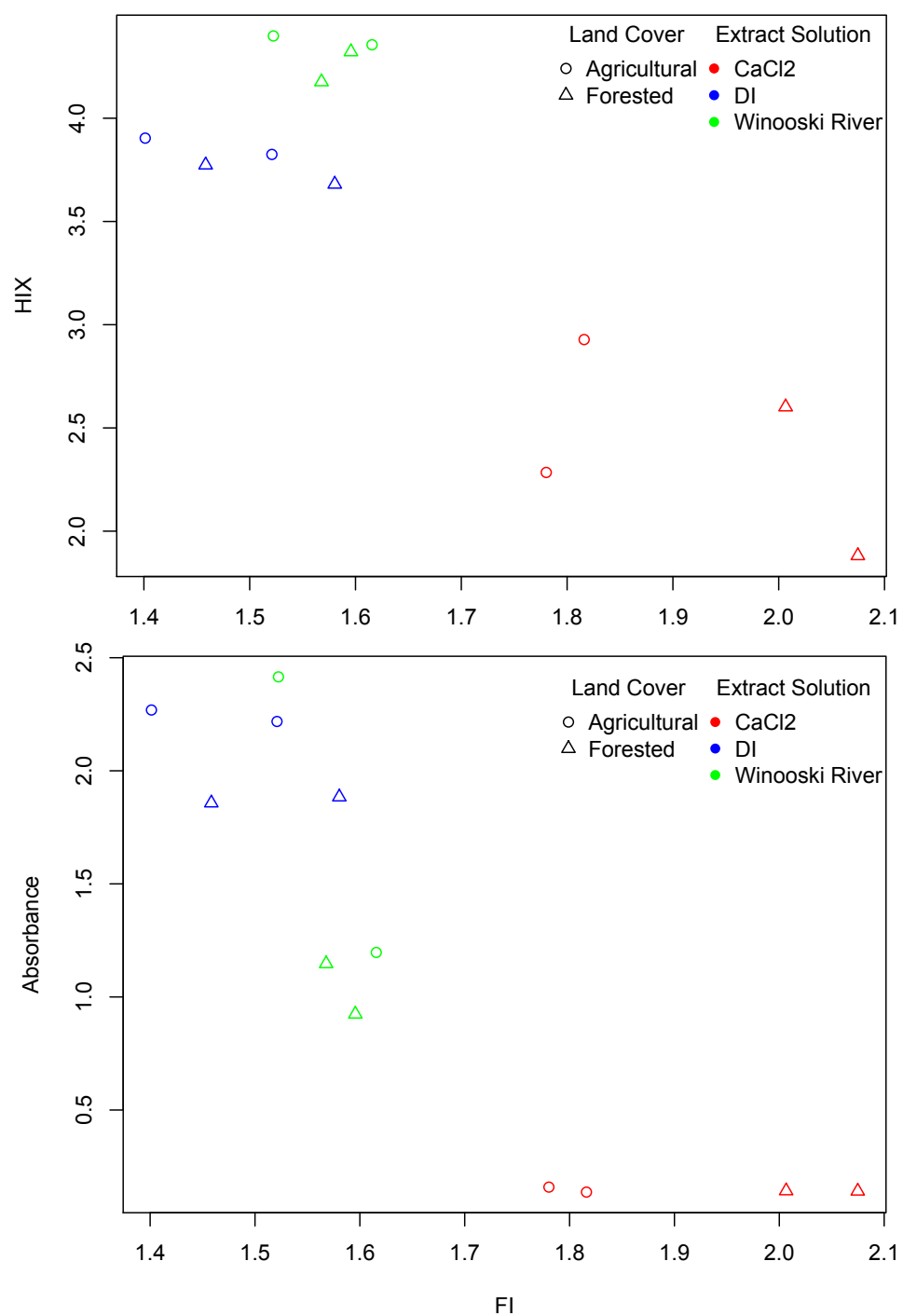


Figure 4.7. FI, HIX, and absorbance at 254 nm, of agricultural and forested soils with three extract solutions.

## 4.4 Discussion

### 4.4.1 Soil Drying In the Laboratory

Although the preparation of laboratory ASE introduces artifacts, it is still an important and widely used method for soil solution analyses, especially when *in situ* sampling is not possible (Swift, 1996). Therefore, it is important to quantify and understand the effect of soil processing and storage on the extracts, including the effects of drying, storage time, and extraction solution.

The comparison between archived soils and the other two treatments is made difficult by the fact that storage time is not the only factor impacting the results. For example, despite careful site selection, it cannot be certain that the exact sample sites were resampled. Furthermore, land use practices may have changed over the two year sampling gap and additionally, short term changes in climate may have impacted soils in that way that differences between archived and newly sampled soils (dry and moist) cannot be clearly related to storage time. However, TOC results are very similar for archived and dry samples (Fig. 5.4), which indicates that at least the characteristics of the total C pool were captured.

Despite these limitations, results presented in this study suggest that drying and storing soils do affect the DOM in the ASE. Both archived and dried soils had similar amounts of the terrestrial components C1 and C3, which were higher than in moist soils, suggesting that drying releases high molecular weight, terrestrial humic compounds. The high C2 in extracts of the archived soil, moderate C2 from the dried soil, and low C2 in the moist soil extracts suggests that the low molecular weight, microbial humic



compounds are released both in the drying process and during storage, suggesting that microbial activity continues during and after the drying process.

The comparison between dry and moist soil, in contrast, is not impacted by these considerations and allows for direct comparison. Several studies have shown that drying of soil greatly increases the organic carbon and nitrogen released upon rewetting (Kaiser et al., 2015; Bartlett and James, 1980). Results presented in this study are in agreement with these findings. For example, extremely high  $SUVA_{254}$  values for the moist samples suggests interference from other light absorbers, such as nitrates and iron. This may indicate high levels of nitrogen released in the extract. Similarly to the study of Zsolnay et al. (1999), the increased DOM released in the aqueous extraction of air dried soils corresponded to an increase in more humified DOM, suggesting the air drying process makes this less bioavailable, more humified organic matter more extractable. In addition, long term storage of the soils results in even more humified DOM, indicating that both drying and storage affect the humification. Conversely, there are more aromatic compounds in the moist soil extracts, as well as more of the C4, tryptophan-like component. This suggests that as soils are dried and stored, the increased WEOC is not derived from an increase in aromatic or protein-like molecules.

Bioavailability is also higher in the dried soils, compared to the moist soils, which may be explained by the higher percentage of humified material and microbial humic C2 component (Boyer and Groffman, 1996). The increase in percent bioavailability in dried soils corresponds with the increase in WEOC, suggesting that the C released during drying is largely bioavailable.

While dried soils release more WEOC than moist soils, the WEOC released from dried soils is correlated with the TOC of the soil. However, WEOC from moist soils is not correlated with TOC. This suggests that TOC could be used to determine the WEOC from dried soils, but not from soils in field moist conditions; the amount of TOC in a soil does not seem to affect the amount leached in field moist conditions.

While laboratory drying of soils alters the C characteristics, in natural conditions, soils also experience drying and rewetting, which could mobilize and leach more WEOC from soils than soils that do not experience drying. Soils that have dried due to exposure will have disrupted aggregates and more C will be accessible and available to the water upon rewetting. Soils that stay moist will not experience this disruption and their C will remain protected by aggregates, unable to be leached. In addition, microbial activity is suppressed in dried soils, while easily degradable material, such as desiccated organisms, accumulates (Zsolnay et al. 1999). When this activity becomes stimulated upon rewetting, this newly available material is easily processed by microbes and available to become WEOC. Therefore, estimating WEOC contribution of a soil depends on the drying and rewetting it has previously experienced.

#### **4.4.2 Effects of Extract Solution**

Previous studies have determined the solution used to extract soils affects the amount and type of C removed from the soil, however consistency in method allows for comparison of soils within a study (Gabor et al., 2015). In the present study,  $\text{CaCl}_2$  solution extract less humified, more microbial OM than DDI or river water (Fig. 5.7), which is in agreement with the stronger microbial signature of salt solution extracts obtained by Gabor et al. (2015). In addition,  $\text{CaCl}_2$  solution extracts less C than the other

solutions, as determined by the low absorbance, as absorbance at 254 nm is used as a proxy for DOC content in stream waters (Deflandre and Gagne, 2001; Spencer et al., 2007).

The  $\text{CaCl}_2$  solution extracts target a different, less humified, pool of C than the DDI and river water extracts, which suggests that the  $\text{Ca}^{2+}$  ion is able to remove C from where it is bound to mineral surfaces. However, the  $\text{Ca}^{2+}$  ion may also be able to assist in the sorption of organic matter to clays in the soil through ionic exchange and bridging (Qualls, 2000). The  $\text{CaCl}_2$  solution has a greater ionic strength than the river water, and is therefore not representative of leaching of soils near a river. In contrast, DDI water extracts have been found to have higher absorbance at 254 nm than extracts using salt solutions, including  $\text{CaCl}_2$ , which may be attributed to the mobilization of highly aromatic compounds (Rennert et al., 2007).

The results indicate that the DDI water and the Winooski River water extract similar amounts of C, although DDI water may extract more WEOC, and the C extracted has similar molecular properties, suggesting that DDI water is a comparable solution to river water in comparing C leaching from soils, as both target the same pools of C in the soil.

While the river water used for this analysis was obtained at baseflow, high flow conditions, which often occur with erosional events, may yield different results, due to the increase in ions, but decrease in ionic strength, in the river. Further studies may quantify the differences between baseflow, higher flow, and other extract solutions and determine how effective ASE are at simulating high flow events.

## 4.5 Conclusions

Drying of soils influences the WEOC pool, as more WEOC is extracted from dried than from field moist soils. Long term storage of dried soils further alters and increases the WEOC pool, while drying and storage time also affect the characteristics of the WEOC, liberating a new pool of humified, microbially processed C. All three sample treatments yield significantly different results, but the archived samples are the most different from the field moist samples, suggesting that long term storage of soils does not preserve DOM in its initial state. The influence of the soil extract is similarly important to the WEOM, as the salt  $\text{CaCl}_2$  solution extracted a different pool of C than the DDI and river water. The DDI and river water extracts contained similar amounts and types of WEOC, indicating that DDI water is an acceptable analogue for leaching with river water.

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## CHAPTER 5: CONCLUSIONS

Using aqueous soil extractions as an analogue for erosional events, land cover was determined to be an important factor in determining SOC in a soil and the potential DOC leached during erosional events and these differences are likely driven at the molecular scale. However, the bioavailability of the C cannot be predicted by land cover or by spectral methods, suggesting that bioavailability must be directly measured, rather than measured by proxy. Further research may be used to use spatially distributed data to generate GIS layers of WEOC amount and type throughout the RC and to further investigate the drivers of bioavailability at the molecular level.

The methods used in this study to simulate erosional events and C leaching from soils are effective for comparison between sites. Drying of soils and long term storage both influence the WEOC pool, liberating a new pool of humified, microbially processed C. The influence of the soil extract is also important to the WEOM, however, the DDI and river water extracts contained similar amounts and types of WEOC, indicating that DDI water is an acceptable analogue for leaching with river water. Further studies are necessary to determine the effects of high flow event stream water as an extraction solution.



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## APPENDIX I: PRELIMINARY DATA USED FOR SAMPLE SITE SELECTION

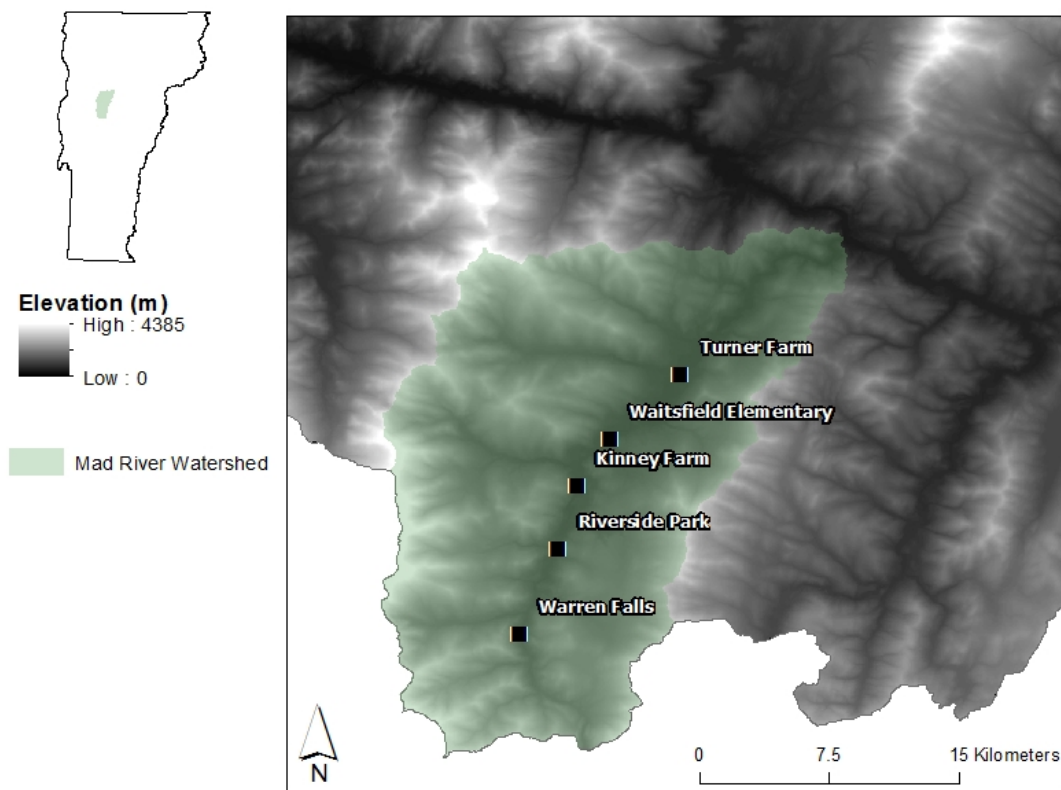


Figure A1. The Mad River corridor, part of the Winooski River watershed, in northern Vermont, including sample sites from the archived samples. Turner Farm, Waitsfield Elementary, and Kinney Farm are agricultural, while Riverside Park and Warren Falls are forested.

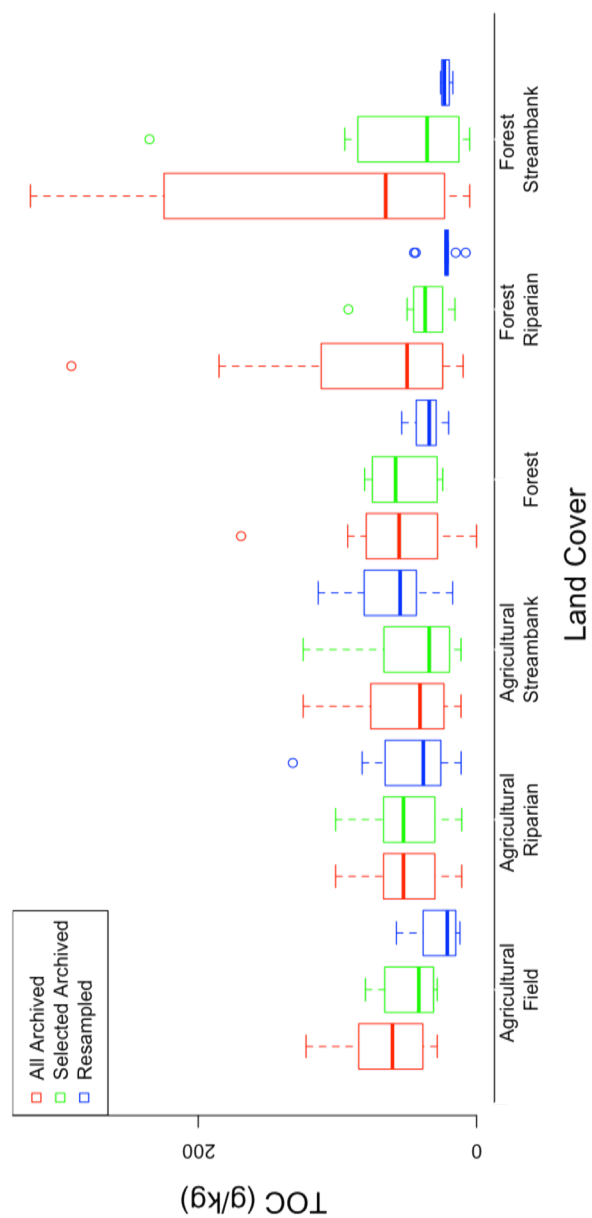


Figure A2. TOC by land cover for all archived soils, archived soils from the sites selected for resampling (Waitsfield Elementary for agricultural and Riverside Park for forested), and resampled soils (at Waitsfield Elementary and Riverside Park). Boxplots show median and upper and lower quartiles in box, range as extended lines.

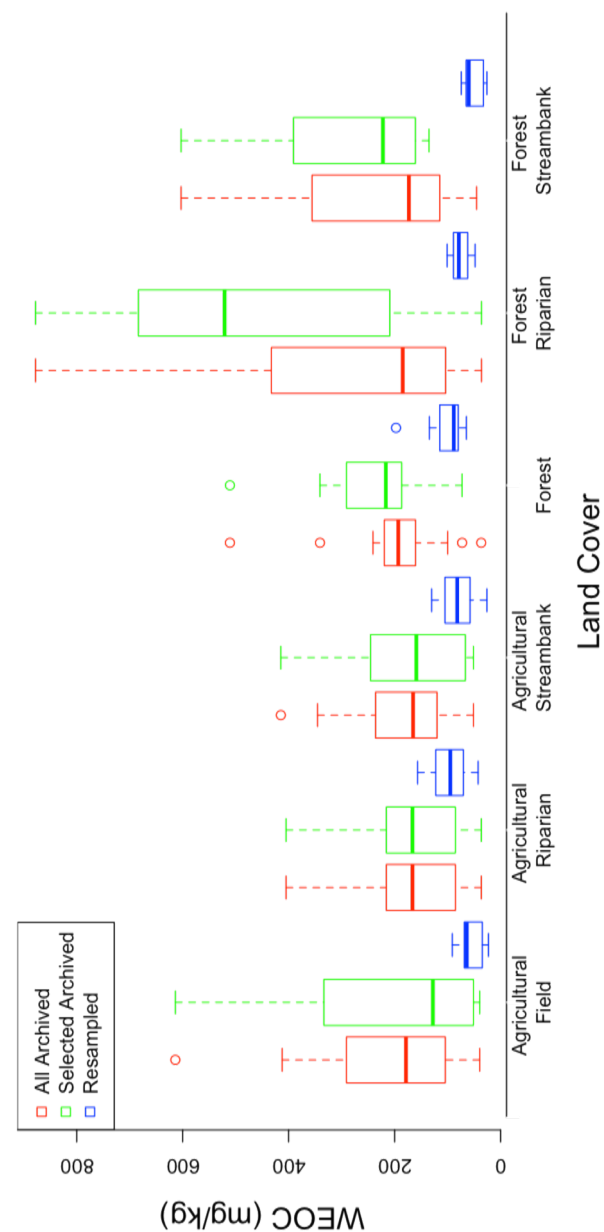


Figure A3. WEOC by land cover for all archived soils, archived soils from the sites selected for resampling (Waitsfield Elementary for agricultural and Riverside Park for forested), and resampled soils (at Waitsfield Elementary and Riverside Park). Boxplots show median and upper and lower quartiles in box, range as extended lines.

## APPENDIX 2: CARBON BY DEPTH

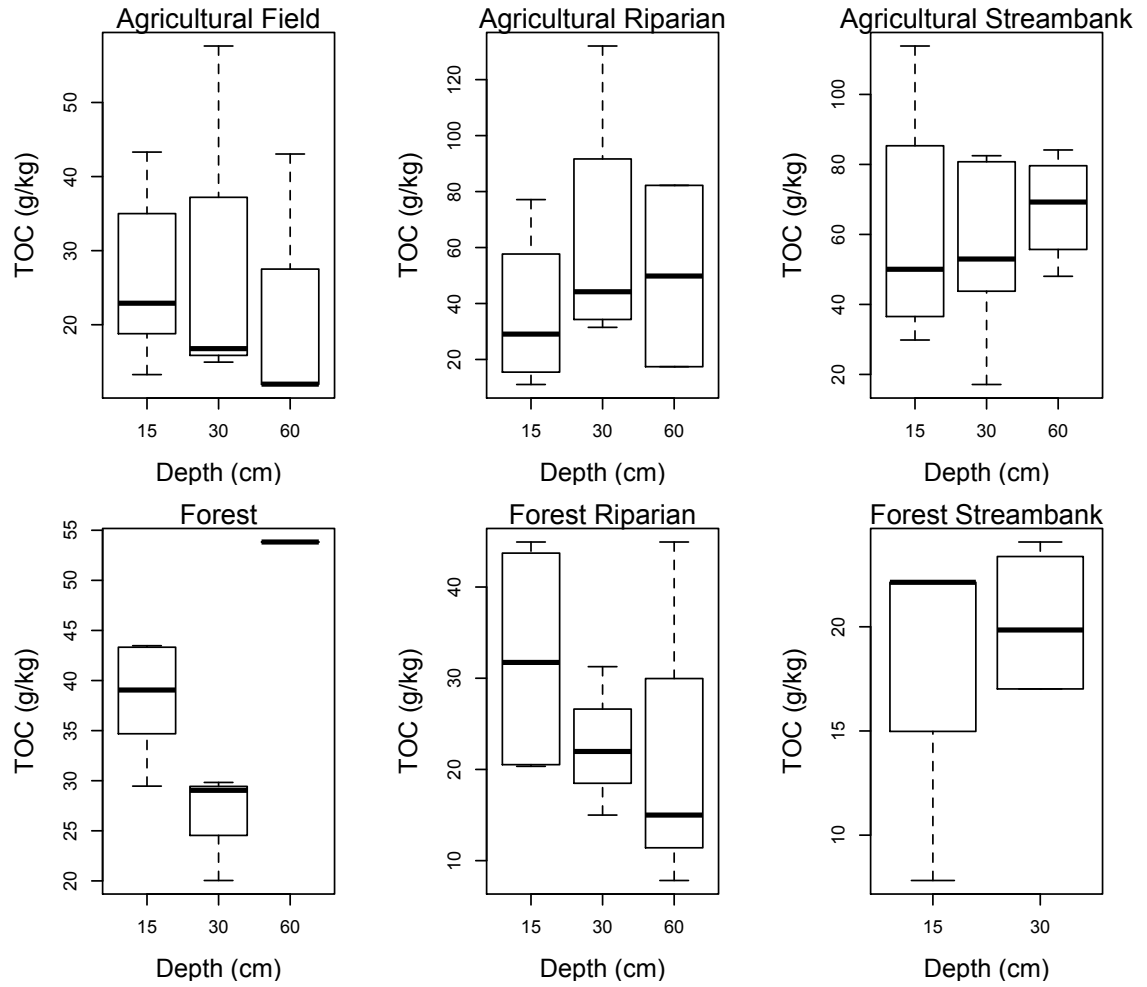


Figure A4. TOC of the soils by sampling depth and land cover.

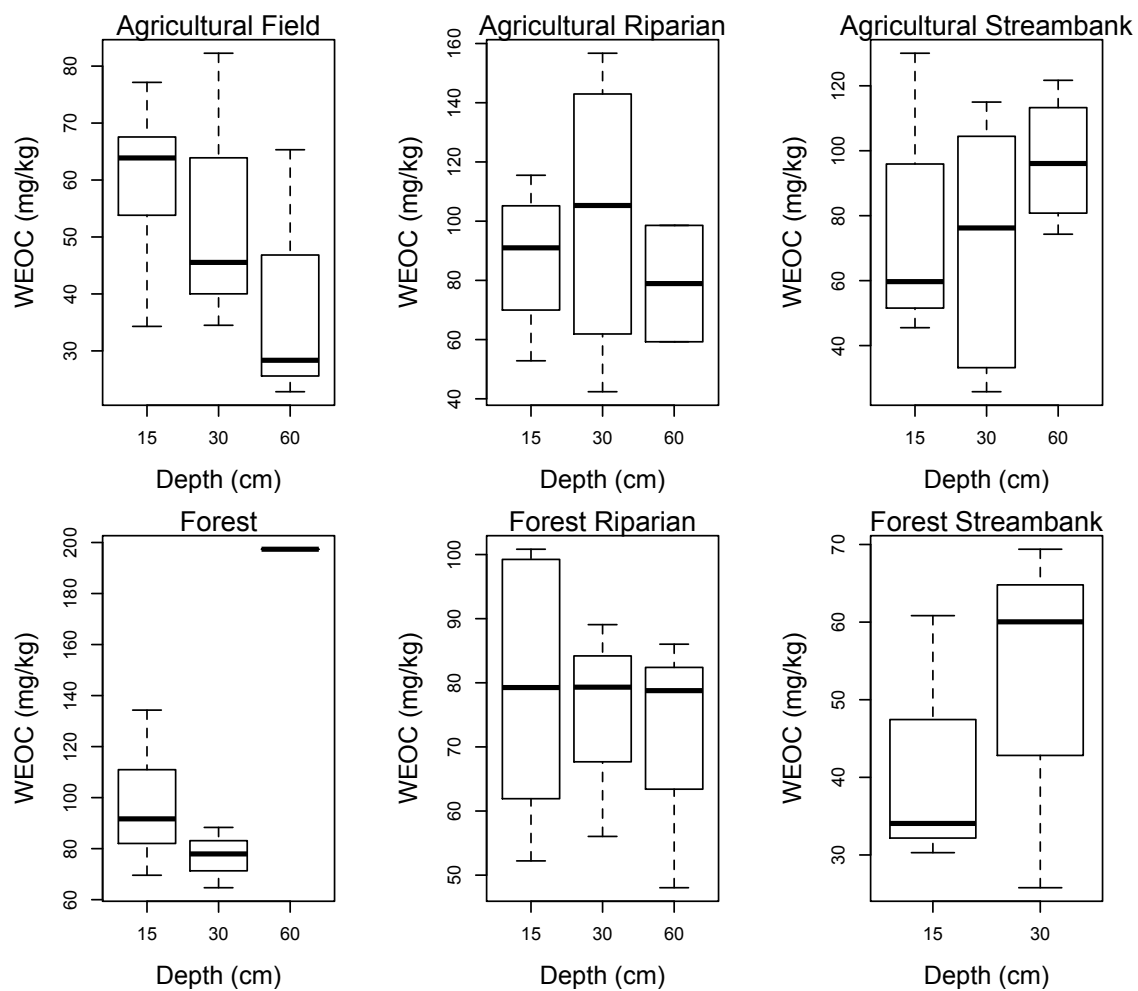


Figure A5. WEOC of the soils by sampling depth and land cover.